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## PREFACE

THE INTERNATIONAL CONFERENCE ON PHYSICS (1934) was organized by the International Union of Pure and Applied Physics and the Physical Society.

Some 200 distinguished physicists attended either as delegates of the National Committees adhering to the Union or as guests of the Conference, invited by the joint Presidents. In addition, membership was open to all interested in Physics; the roll of members contained over 600 names.

The meetings in London were held either in the rooms of the Royal Society, Burlington House, or at the Royal Institution of Great Britain.

The Conference also met at Cambridge on Thursday, October 4th, by the invitation of Lord Rutherford.

The papers read before the Conference, with contributions to the discussions made either at the meetings or subsequently, are being published in full in two volumes:

Vol. I. Nuclear Physics.

Vol. II. The Solid State of Matter.



# CONTENTS

## VOLUME I

		PAGE
1. ADDRESS OF WELCOME	<i>Sir F. Gowland Hopkins</i>	I
2. OPENING SURVEY	<i>Lord Rutherford</i>	4
3. GENERAL QUANTUM THEORY		
Quantum Electrodynamics	<i>M. Born</i>	19
4. NATURAL $\beta$ -DECAY		
Report on Theoretical Considerations on the Radio-active $\beta$ -decay	<i>G. Beck</i>	31
The $\beta$ -ray Type of Radioactive Disintegration	<i>C. D. Ellis</i>	43
General Stability Problems of Atomic Nuclei	<i>G. Gamow</i>	60
Discussion on Natural $\beta$ -decay	<i>H. A. Bethe;</i>	66
<i>W. M. Elsasser; E. Fermi; H. O. W. Richardson; K. Sitte</i>		
5 (a). ARTIFICIAL RADIOACTIVITY		
Artificial Radioactivity Produced by Neutron Bombardment	<i>E. Fermi</i>	75
Artificially Produced Radio-elements	<i>Mons. and Mme Joliot</i>	78
Discussion on Artificial Radioactivity	<i>J. D. Cockcroft;</i>	
<i>S. Maracineanu; J. C. McLennan, L. G. Grimmett and J. Read;</i>		
<i>L. Szilard</i>		
5 (b). DISINTEGRATION AND SYNTHESIS OF NUCLEI AND ELEMENTARY PARTICLES		
Photoelectric Disintegration of the Diplon	<i>H. A. Bethe and R. Peierls</i>	93
Nuclear Transformations Produced by $\alpha$ particles and Neutrons. With Plate I	<i>J. Chadwick and N. Feather</i>	95
Transmutations Produced by High-speed Protons and Diplons. Part I	<i>J. D. Cockcroft</i>	112
Gamma-rays from Artificially Produced Nuclear Transmutations	<i>H. R. Crane and C. C. Lauritsen</i>	130

	PAGE
5 (b). DISINTEGRATION AND SYNTHESIS OF NUCLEI AND ELEMENTARY PARTICLES ( <i>continued</i> )	
Transformation Effects Produced in Lithium, Heavy Hydrogen and Beryllium by Bombardment with Hydrogen Ions	<i>M. L. E. Oliphant</i> 144
Discussion on Disintegration and Synthesis of Particles	<i>Lord Rutherford;</i> 162
<i>H. A. Bethe; J. Chadwick; L. R. Hafstad; W. R. Hartree;</i>	
<i>M. Goldhaber;</i>	<i>H. S. W. Massey</i>
6. COSMIC RADIATION	
Fundamental Processes in the Absorption of Cosmic-ray Electrons and Photons	<i>C. D. Anderson and S. H. Neddermeyer</i> 171
The Latitude Effect for Cosmic Rays	<i>P. Auger and L. Leprince-Ringuet</i> 188
Some Measurements of Cosmic Radiation at High Altitudes	<i>P. Auger and L. Leprince-Ringuet</i> 195
The Absorption of Cosmic Rays	<i>P. M. S. Blackett</i> 199
A Very High Altitude Survey of the Effect of Latitude upon Cosmic-ray Intensities and an Attempt at a General Interpretation of Cosmic-ray Phenomena	<i>I. S. Bowen, R. A. Millikan and H. V. Neher</i> 206
A Study of Cosmic-ray Bursts at Different Altitudes	<i>A. H. Compton and R. D. Bennett</i> 225
The Connexion between Cosmic Radiation and Atomic Disintegration	<i>G. Hoffmann</i> 226
Some Results Arising from the Study of Cosmic Rays	<i>B. Rossi</i> 233
Discussion on Cosmic Radiation	<i>G. Bernardini;</i> 247
<i>H. A. Bethe; C. W. Gilbert; V. Posejpal; E. Regener; D. Skobel'tzyn</i>	

# ADDRESS OF WELCOME

BY SIR FREDERICK GOWLAND HOPKINS

M.A., D.Sc., LL.D., F.R.C.P.

*President of the Royal Society*

As your Chairman has told you, Ladies and Gentlemen, I am entrusted with the pleasant and very enviable task of offering, on behalf of the Royal Society of London, which I represent, a few words of hearty welcome to all members of this Congress. To those great investigators who have travelled from abroad to assist the business of this Conference and by their personal presence to add so much to its interest, I would like to offer a special word of thanks.

As you are aware, this is a joint Conference of the International Union of Pure and Applied Physics, and the Physical Society. You may also be aware, or I would remind you, that the International Union itself was the outcome of an International Conference held in the rooms of the Royal Society in October 1918. At that Conference an International Council was formed for the encouragement of international co-operation in scientific work, and under it some seven specialist unions are now active, and of these one is that of Pure and Applied Physics.

Now the Royal Society, for the first two centuries of its existence, was the sole, or almost the sole channel, through which the results of English scientific work were published to the world, but with the increasing pressure of specialization, specialist societies took birth, of which the Royal Society can claim to be the parent. Of these, the Physical Society was one; it came into existence some sixty-six years ago and is now a very active, flourishing society with over 1000 members, and it is no secret that it was due to the active spirit of the Physical Society that the conception of this Conference arose.

Before I venture, if I dare venture, on any reference to the work of this Conference, I hope you will understand that my qualifications for addressing you are entirely *ex officio*, and in no sense personal. I enjoy the great privilege of being President of the Royal Society, and it is as its official representative, and only so, that I am entitled to speak. It is, I cannot but feel, somewhat unfortunate for the Royal Society that at the moment of this important Conference the occupant of its presi-



dential chair should chance to be a biologist instead of a physicist, but believe me, every Fellow of the Society, and indeed every British scientific worker, whatever his qualifications, will take the deepest interest in your proceedings, and at least do his best to understand them. Even the intelligent lay public, I think, though I fear not greatly helped to an understanding by the lay Press, will find itself also trying to follow all that is said in your meetings.

If I might for a moment refer to the biologist in particular, I think he is apt just now to wonder how far the growing revelation of atomic properties will come to bear on his own problems; so rapidly are these revelations now occurring that he may fear to wake up some morning and find that some atomic property promises to throw more light on the problems of Life than his own methods have ever done; and he will even feel, perhaps, that his methods are no longer those which should be followed. This however is not yet a conviction and the revelation has not yet arrived. No section is to deal on this occasion with the mysteries of life, but you are to deal with matters that were mysterious enough to my generation when it was young. Your main discussions are to be concerned with nuclear physics and with the properties of the solid state, two regions in which till a short time ago Nature seemed to be met with in her most secretive and recalcitrant moods. But how astonishingly rapid has been the progress which is now revealing the secrets of those regions. Almost every year during the past few decades has seemed to yield a harvest of knowledge enough to make it remarkable; but the harvest of this year surely has made it in very truth an *annus mirabilis*. It seems but yesterday that the atom was thought to be made up of protons and electrons alone; now we hear of the properties of neutrons, positrons, photons, and possibly, I am told, also of neutrinos. More, we have made the acquaintance of artificial radio-active substances and even of atoms new to the universe. In the case of our knowledge of the solid state, progress has surely also been rapid beyond all expectation. The Conference certainly will have much to discuss.

This, Ladies and Gentlemen, is the first time that a Conference of this sort has been held in this country. You will admit, I feel sure, that it is a country well entitled to entertain the Physicists of the world. It is the land of Newton, who still stands high upon his pedestal and will remain there for all time; it is able to offer you as a meeting place the theatre where Faraday taught, adjacent to the laboratories in which his great work was done; it is the country of Boyle, Cavendish, Clerk Maxwell

and Kelvin, Rayleigh and Crookes. But even more significant to this Conference, it is the country of Joseph Thomson, and of Rutherford, great pioneers and still strong living forces. In the region of your other special interest, is England not the home of the Braggs, father and son?

What cannot fail to appeal to all here however is a realization of the fact that the extraordinary increase of knowledge which we are experiencing, including the very avalanche of new facts which the last few months has brought, has not come from the work of any one nation but from those of many. Science, after all, is always international in its progress. Taking the papers announced for this Conference in the order in which they appear in the programme, we find that they emanate from Germany, England, the United States, Czecho-Slovakia, France, Italy, Russia, Switzerland and Holland—surely an international programme. It is very remarkable also that this great advance in those two important aspects of science with which you are to deal has gone on in spite of political unrest, financial stringency and more unfortunate than all, perhaps, anti-intellectual movements in the world. This remarkable progress, we rejoice to realize, has occurred in spite of all such hindrances. It is due to that sheer thirst for knowledge, to the divine curiosity which rise superior to external circumstances.

I will not attempt to mention the names of the distinguished investigators who are to contribute to your discussions. Many are known to most, and all will become better known as the Conference proceeds; but piety, respect for a great woman, the greatest investigator that her sex has yet included—Madame Curie—makes me venture to express (and I am sure you will all agree with me when I do express) the extreme pleasure we feel that M. Joliot and Mme Curie-Joliot are to take part in our discussions.

I must not forget that the International Union has certain special practical problems to discuss, and we may well hope that from their discussions here, agreement on very many important points will be reached.

I will lastly congratulate the sections on the Presidents under whom they are to sit—Professor Millikan and Lord Rayleigh—and I will finish by once more offering on behalf of the Royal Society a most hearty welcome to the Congress as a whole.

# OPENING SURVEY

BY LORD RUTHERFORD

O.M., F.R.S.

Cambridge

I HAVE PROMISED on this occasion to make some general remarks on the origin and development of our knowledge of atomic nuclei. I need hardly say that this has been to me a subject of intense interest, for most of my investigations have been concerned with this fundamental problem.

In surveying the history of this development, one cannot but recognize how much of our knowledge has been derived from a study of the radioactive bodies and from the utilization of the energetic  $\alpha$ -particles and  $\gamma$ -rays spontaneously emitted from these elements. The interpretation of the radioactivity of uranium and thorium gave us for the first time definite proof that the atoms of these elements are unstable and break up with explosive violence, giving rise to a long series of successive transformations. The study of the radiations emitted during these atomic explosions brought out in striking fashion the enormous emission of energy in many of these transformations. While we are able to watch these surprising atomic explosions, unfortunately we are unable to control them by any forces at our command. For this reason, further progress seemed difficult when once the main series of transformations had been established. A wealth of new facts was accumulated, but our knowledge of atomic structure was too vague at that time to hope to interpret them except on broad general lines.

Fortunately, however, another direction of attack was possible. The radioactive bodies provide us with a stream of swift projectiles— $\alpha$ -particles—with which to bombard other atoms and to study the effects produced. The  $\alpha$ -particle has so great an energy of motion that it is able to penetrate deeply into the structure of atoms in its path and thus might be expected to give us some information on the intensity of the electrical forces existing in the atom. The study of the large deflections of  $\alpha$ -particles from a single encounter with an atom disclosed the existence of intense electric fields within the atom. In order to interpret these observations, I put forward in 1911 the theory of the nuclear structure of

all atoms. On this new theory the ordinary physical and chemical properties of an atom, apart from its mass, are defined by a whole number, representing the number of electronic units of charge carried by the minute nucleus. The laws of scattering predicted on this theory were completely confirmed by the fine experiments of Geiger and Marsden in 1912. They were able to show that the charge on the nucleus is approximately equal to half its atomic weight. At that time Geiger and Marsden, and Bohr and Moseley were working in my Laboratory at Manchester. Bohr assumed the correctness of the nuclear theory and applied it in 1913 in his theory of the origin of spectra, the remarkable consequences of which are so well known to all physicists. Bohr was the first to suggest that the nuclear charge is given by the atomic or ordinal number of the element. He was the first also to point out that a clear-cut distinction should be drawn between the nuclear and extra-nuclear properties of an atom. The property of radioactivity is to be ascribed to the nucleus, while the ordinary light and X-ray spectra originate in disturbances of the outer electrons which surround the nucleus at a distance.

The next great step in advance was made by Moseley in 1913 as the result of a study of the X-ray spectra of the elements. It is of interest to record that Moseley undertook this investigation with the express purpose of obtaining a definite decision whether the properties of an element depend on its atomic weight, as supposed at that time, or are defined by a whole number representing its nuclear charge. The results obtained in his pioneer investigations are of outstanding importance and constitute a veritable landmark in the history of our knowledge of atomic nuclei. He showed not only that the properties of an atom are defined by the atomic or ordinal number of the element, but that with few exceptions all numbers are represented by known elements between hydrogen 1 and the heaviest element uranium 92. The X-ray spectra of the missing elements could be accurately predicted and have formed an invaluable and successful guide in the search for the elements unknown at that time. Guided by the nuclear theory and Bohr's theory of spectra, he interpreted his results by assuming that the ordinal number of an element is a measure of its nuclear charge. The correctness of this view was later substantiated by Chadwick in 1920 by direct measurement of the nuclear charge from observations on the scattering of  $\alpha$ -particles. It has always seemed to me a remarkable fact that, apart from the radioactive nuclei, practically all nuclear charges are represented by known and stable elements. It might

have been anticipated that atoms of certain nuclear charges might be unstable and break up, leaving gaps in the order of the elements. Recent observations on the artificial transmutation of elements certainly show that unstable isotopes of certain elements can be formed under some circumstances, but in general one or more isotopes of each element appear to be permanently stable.

### *Isotopes*

While the discovery of Moseley fixes finally the number of elements between hydrogen and uranium, it throws no light on the number of species of atoms of different masses that may exist with the same nuclear charge. On the nuclear theory, such atoms should show almost identical physical and chemical properties apart from properties like diffusion, which depend directly on the mass of the atom. The line spectrum of the atom should differ only to a slight degree with the change of its nuclear mass. Even in the case of the recently discovered atom of hydrogen of mass 2, the Balmer lines differ in wave-length only by one part in 3700 from those of ordinary hydrogen. The wide difference in mass between  $H=1$  and  $H=2$  is responsible for the apparent differences of physical properties, and is responsible for the possibility of the separation of the heavier isotope by electrolysis and other methods.

The discovery of the complexity of the chemical elements by Soddy is a contribution of fundamental importance. The first definite evidence of this complexity was obtained from a study of the chemical properties of the radioactive bodies. Certain elements, which showed distinctive radioactive properties, were found to be inseparable by chemical methods and had apparently identical chemical properties. Such chemically indistinguishable elements were called "isotopes" by Soddy. A great advance was made when Aston devised an ingenious method for determining the isotopic constitution of the ordinary elements. The great majority of the elements were found to be complex, consisting of a mixture of two or more isotopes, and the relative abundance of each isotope could be measured. More than 200 species of elements are now known, and no doubt this number will be substantially increased in the near future. Optical methods have been found very valuable in detecting the presence of isotopes existing in small abundance in light elements like carbon, nitrogen and oxygen. Apart from the remarkable difference in the number of isotopes shown by even and odd numbered elements, the most significant fact observed by Aston is expressed by the well-known "whole

number rule." The masses of the isotopes of all the elements were found to be nearly whole numbers expressed in terms of the oxygen atom of mass 16. This indicated that a nucleus of mass nearly unity entered into the structure of all heavy nuclei. This was given the name "proton" and was assumed to be the hydrogen nucleus, the difference of mass being ascribed to the so-called "packing effect." We now know that the neutron of mass nearly the same as the proton is also an important constituent of nuclei, and probably these two units, the proton and the neutron, form the essential entities from which complex nuclei are built up.

While in general the atomic masses of all the isotopes are integral numbers in terms of  $O = 16$ , yet this rule, while of great use as a working guide, is only approximate. From the accurate measurements of Aston we know the general trend of the departures from the whole number rule with increasing weight of the atom. It is now of great importance that the masses of all the isotopes should be known with the highest possible precision, for in a sense the mass is a measure of the energy of the atom. The interpretation of the possible modes of transformation of an atom depends to a large extent on the accuracy with which the relative masses are known. It is now increasingly clear that the general law of the conservation of energy holds at any rate for most transformations that have been examined. Conversely, when the mode of transformation can be clearly demonstrated, it is possible to fix the masses of some of the atoms with even greater precision than by means of the types of mass spectrograph used by Aston and Bainbridge. I shall refer later to recent experiments in which it has been found possible to produce unstable isotopes which break up in novel ways.

### *The Transmutation of the Elements*

I have so far given a brief account of the methods of enumerating the different types of nuclei in the earth and the accurate determination of their relative masses. Apart from the radioactive elements of high atomic weight and a few other weakly radioactive elements like potassium, rubidium and samarium, the majority of the elements appear to be permanently stable and under normal conditions on the earth suffer no appreciable change over periods long compared with the age of our earth. This stability of so many varied nuclear structures has always seemed to me a most surprising fact. It seemed clear from the first that the nucleus of an atom must be held together by very powerful forces, and its disruption could only be accomplished by the use of very powerful and

concentrated sources of energy. In order to form some idea of the magnitude of nuclei and of the nature of the forces in their neighbourhood, in conjunction with Chadwick a number of observations were made on the scattering of  $\alpha$ -particles by light elements like hydrogen, helium and aluminium at close distances of approach. The scattering of  $\alpha$ -particles was found to be abnormal, indicating the presence of deflecting fields near the nucleus varying more rapidly than the inverse square law. It was in general supposed that intense attractive forces on the  $\alpha$ -particle came into prominence for short distances. These results can now be interpreted on the same general lines, but with much more definiteness, by the application of the ideas of wave mechanics.

If a veritable transformation of the atom was to be effected, it became clear that the charge on the nucleus must be changed either by the addition or subtraction of a charged particle. The use of the swift  $\alpha$ -particle to bombard the atoms of matter seemed to be the most promising line of attack. Even if the  $\alpha$ -particle was unable to overcome the repulsive fields and penetrate the nucleus, it must approach so closely to the nucleus as to be able to distort its structure and possibly to effect a disruption into its component parts. The first clear proof of the artificial transformation of an element was obtained in 1919 when  $\alpha$ -particles were used to bombard nitrogen. Protons were found to be ejected with high speed. Later, in conjunction with Chadwick, twelve light elements were found to undergo transformation by  $\alpha$ -particle bombardment, and in all cases swift protons were emitted. The mechanism of the transformation of nitrogen was made clear by Blackett in 1925 by photographing in an expansion chamber the tracks produced in a disintegrating collision. It was seen that the  $\alpha$ -particle was captured by the nitrogen nucleus leading to the expulsion of a swift proton and the probable formation of an isotope of oxygen of mass 17. Incidentally, it should be mentioned that at that time no such isotope had been observed in ordinary oxygen. It seems likely that a similar process occurs in all the twelve light elements transformed by  $\alpha$ -particle bombardment. The  $\alpha$ -particle is captured and a proton ejected, leaving behind a new nucleus of charge one unit higher and a mass 3 units greater than that of the struck nucleus.

The proof of these transformations, which are on a very small scale, was only made possible by the powerful methods developed for counting single atoms in motion. The scintillation method was first employed for the detection of the swift protons which appeared to be ejected over a wide range of speed. The use of polonium as a strong source of  $\alpha$ -particles,

free from the disturbance due to the action of  $\beta$ - and  $\gamma$ -rays, made possible the use of electrical methods of counting protons. By these means, Pose observed that the protons appeared to be emitted in groups of definite speed. This important observation has been followed up by Chadwick and many other workers and has led to a much clearer understanding of the processes that may occur during a transformation. For example, in the case of aluminium, a number of definite resonance levels have been observed in each of which there is a high probability of the capture of an  $\alpha$ -particle of characteristic speed. It also seems clear that there is a close correlation between the difference of energies of the various proton groups and the energy of  $\gamma$ -rays which are emitted during these transformations. Investigations of this kind are of great importance in giving us some indication of the structure of nuclei and of their energy levels.

### *The Neutron*

A close examination of the transformations produced by  $\alpha$ -rays has led to another discovery of far-reaching importance. Bothe in 1930 observed that beryllium when bombarded by  $\alpha$ -rays did not emit any protons, but gave rise to a marked penetrating radiation which appeared to be of the  $\gamma$ -ray type. In the subsequent examination of this effect by M. and Mme Curie-Joliot and Chadwick in 1932, it became clear that an important part of this radiation consisted of a stream of swift uncharged particles called neutrons, which have a mass about the same as that of the proton in the free state. The neutron does not itself ionize the gas in its path, but only shows its presence by the recoil of the nucleus with which it collides. This strange type of particle is in itself an important agent in effecting the transformation of other nuclei in novel ways, as has been shown by Feather, Harkins, Fermi and others. It has now become clear that the neutron plays a very important part as a unit in the structure of nuclei. So far only neutrons of mass about 1 have been observed, but it may be that neutrons of mass 2 or more are produced under some circumstances.

### *Artificial Radioactivity*

Still another discovery of much interest has emerged from a study of the effects produced by the bombardment of atoms by  $\alpha$ -particles. In the types of transformation so far considered, the final products of the transformation were believed to be stable isotopes of one of the elements.



In certain cases, M. and Mme Curie-Joliot found in 1933 that unstable isotopes were produced which broke up according to the same laws as a radioactive body and with a characteristic period. Strange to say, a positive and not a negative electron is emitted in the transformations. By these methods, definite evidence has been obtained that unstable isotopes of nitrogen, silicon and phosphorus are produced. This was the first proof of the artificial production of a radioactive element. Since that time, it has been found that similar radioactive isotopes can be produced by bombardment of matter by fast protons and diplons. The effect of the  $\alpha$ -rays is confined to the lighter elements, but this new method of attack has recently been greatly extended by Fermi, Segre and others in 1934 using neutrons instead of  $\alpha$ -particles. The neutron is able to pass freely into the structure of even the heaviest nuclei and may produce a transformation. In this way, Fermi has succeeded in producing a large number of new radioactive isotopes. Apparently in the majority of cases,  $\beta$ -particles and not positrons are emitted. No doubt a large amount of work will be required to make certain of the mechanism of the transformations that give rise to these new radioactive bodies, but this new method of attack is of much promise since it can be applied with success to even the heaviest nuclei.

### *Transformations by Protons and Diplons*

So far we have considered the transformations produced by fast  $\alpha$ -particles, which are themselves derived from the spontaneous transformation of the radio-elements, and also by neutrons, which are in turn a product of the transformation of certain elements bombarded by  $\alpha$ -particles. In general for  $\alpha$ -particles of energy 8 million volts, about 1 particle in  $10^5$  or  $10^6$  is able to effect a transformation in the nucleus of a light element. The efficiency of the fast neutron in producing a transformation is much higher than that of the  $\alpha$ -particle and in some cases may approach unity.

In order to widen the range of these investigations, it was early recognized that much more intense streams of swift projectiles of different kinds were desirable for bombarding purposes. Such intense streams of charged particles can be readily produced by the passage of an electrical discharge through gases at low pressures and acceleration in a vacuum by the application of high voltages. From considerations of the transformation effects produced by  $\alpha$ -particles, it was at first natural to suppose on classical views that the bombarding particles should have an energy

of several million volts to be effective. The problem changed its aspect when Gamow showed that on the ideas of the wave mechanics there was a finite if small probability that a particle of quite low energy should penetrate a nucleus. A number of investigations both in Europe and America were made to develop methods of producing streams of fast particles for bombarding purposes. The first successful application of this new method was made by Cockcroft and Walton in 1932. They found that a stream of protons of energy about 300,000 volts was able to produce transformations on a marked scale in the light elements lithium and boron, fast  $\alpha$ -particles being liberated in large numbers. It became clear that the nucleus of lithium of mass 7 occasionally captured a proton and broke up into two  $\alpha$ -particles expelled with equal speed in nearly opposite directions. The correctness of this view was confirmed by Kirchner, and Dee and Walton, by photographing the tracks of the  $\alpha$ -particles in an expansion chamber. The efficiency of the transformation increased rapidly with increase of energy of the bombarding protons. By using an intense stream of protons, Oliphant and others found that transformation was produced using protons of energy as low as 20,000 volts. Oliphant showed that the isotope of lithium of mass 6 under proton bombardment gave rise to two groups of particles of different range. It is believed that this nucleus captures a proton and then breaks up into an  $\alpha$ -particle and a new helium nucleus of mass 3. In the case of boron, it seems likely that the isotope of mass 11 captures a proton and then breaks up into three  $\alpha$ -particles.

An unexpected development of these methods was made possible by the discovery and separation of the isotope of hydrogen of mass 2. Lawrence of the University of California had devised an ingenious method of multiple acceleration to obtain projectiles with an energy as high as 3 million volts. He found that the ions of heavy hydrogen—called deuterons or diplons—were at least 10 times more efficient than protons of equal energy in producing transformations of a novel kind in many light elements. In the case of lithium, for example, not only are very high speed  $\alpha$ -particles produced but also protons and neutrons. In several cases, a single element gives rise to a number of discrete groups of protons. Lauritsen, Crane and Lawrence have found that neutrons are liberated in quantity from several elements. In the bombardment of fluorine by diplons,  $\gamma$ -rays of high quantum energy are emitted.

It seems clear that in some cases a number of distinct types of transformation occur in a single nucleus. No doubt the possible mechanism

of these transformations will be discussed in detail at this Conference, but I must refer in passing to the striking results which have been observed by Oliphant and Harteck when diplons are used to bombard compounds containing heavy hydrogen. In these nuclear reactions, it has been found that a new isotope of hydrogen of mass 3 is formed and also a helium nucleus of mass 3, while neutrons are emitted in great number. The production of these two isotopes by dipton bombardment of heavy hydrogen has been confirmed by Bleakeney and Harnwell by direct physical and chemical methods. The efficiency of these transformations is high and the effects can be conveniently studied with diplons of energies about 100,000 volts.

The high efficiency of the dipton compared with the proton in effecting transformations is a matter of some surprise. On the theory of Gamow, it is to be expected that for equal energies, the frequency of penetration of the nucleus would be much greater for protons than diplons—the reverse to what is observed. It may be that the great majority of the protons which enter a nucleus escape again without producing a transformation. On the other hand, it is very likely that the dipton on entering the intense fields inside the nucleus is broken up into a proton and neutron and that a transformation follows in the great majority of cases if the energy conditions make it possible.

So far, definite proof of transformations of light elements has been obtained with protons, diplons and helium nuclei as bombarding particles. No doubt in the near future observations will be made of the effect of other projectiles like the nuclei of lithium, boron and other light elements.

### *Transformations by other Agencies*

So far, no definite information has been obtained that fast electrons, whether positive or negative, are able to produce transformations. The experiments to test this point will be technically difficult on account of the intense X-radiation generated by bombardment of the target.

It is to be anticipated that high frequency  $\gamma$ -radiation should prove effective in causing transformations. The first evidence in this direction has recently been obtained (1934) by Chadwick and Goldhaber. Heavy hydrogen gas was exposed to the action of the high energy  $\gamma$ -rays from thorium C'. It seems clear that under these conditions the dipton is occasionally broken up into a proton and neutron. This observation should provide an accurate method for determining the mass of the

neutron. The results so far obtained by this method indicate a value between 1.0075 and 1.0085.

The study of the effects of high frequency X-radiation on a nucleus promises to open up a new and important means for throwing light on nuclear processes.

The most energetic particle so far used in studying transformations is the  $\alpha$ -particle from thorium C' of energy nearly 9 million volts. It will be of great interest to examine the effects of different projectiles of much higher energy. The swiftest particles known accompany the cosmic rays, and it is clear that many of the particles, whether electrons, positrons or protons, have energies of the order of 100 million volts, while some are believed to have energies even greater than 1000 million volts. We shall no doubt hear later in this Conference the evidence in support of the view that these swift particles and the high frequency radiation that is probably present are able to disrupt atomic nuclei. Information of this kind is of great value, for it is unlikely that we shall ever be able to produce particles of such great energy in the laboratory.

The first evidence of the existence of the positive electron or positron was obtained by Anderson and Blackett in 1933 from a study of the cosmic rays, and it will be of much importance to study the effects produced in nuclei by such fast electronic projectiles. It may be that the transformation effects of a very energetic projectile may be very different from that of the same projectile endowed with much less energy. The energy of the swifter particles is ample in some cases to break up a heavy nucleus into its ultimate components.

### *Summary*

After the first discovery of artificial transmutation by the action of  $\alpha$ -rays progress was at first slow, but has rapidly accelerated during the past few years. The subject has opened up rapidly and has led to a number of important fundamental advances. It has led to the discovery of the neutron and positron as fundamental units in the structure of matter, and has proved the existence of new stable nuclei like the isotope of hydrogen of mass 3 and the isotope of helium of mass 3, as well as a large number of unstable nuclei which behave like radioactive bodies. The study of the transformation of elements by artificially produced fast particles like the proton and dipion has given us a wealth of new data which is still in process of interpretation. Many researches are in progress in various parts of the world to devise simple and efficient methods of

production of intense streams of fast projectiles for transformation purposes. There are now many skilled workers in this field and we may consequently expect large additions to our knowledge of atomic nuclei during the next decade.

The rapidity of advance in the last few years has been in large part due to the great improvement in the technical methods of attack. Largely due to the work of Geiger, Greinacher, Wynn-Williams and others, we have now available simple and reliable methods for automatically counting swift particles like  $\alpha$ -particles and protons. The sensitive Geiger-Müller tube counters have proved of the utmost value in the study of the cosmic rays and in investigating the production of radioactive bodies by artificial methods, and science owes a great debt of gratitude to C. T. R. Wilson for the invention of that wonderful instrument, the expansion chamber. This has proved a powerful method for investigating the nature of the cosmic rays and the transformation of the elements. In many cases it affords in a sense a final court of appeal by which the validity of our explanations can be judged.

The use in the laboratory of high voltages of the order of a million volts to accelerate projectiles has raised many difficult technical as well as financial problems. We owe much to those pioneers like Coolidge, Allibone, Tuve, Lauritsen, Brasch and Lange and others who have opened up these new methods of attack. Progress in this direction would have been very difficult if not impossible but for the invention of fast diffusion pumps in which Gaede was the pioneer. The invention by Van der Graaf of a new type of electrostatic machine for the production of very high voltages may prove of much importance for the future. We must not omit to mention our appreciation of the skill of Lawrence in developing to a successful issue his method of multiple acceleration which has given us the fastest particles so far generated in the laboratory.

### *Constitution of Nuclei*

The spontaneous emission of  $\alpha$ -particles and electrons from the radio elements and the expulsion of protons from many light elements bombarded by  $\alpha$ -particles, together with the results of Aston on the masses of the isotopes, early led to the belief that the nuclei of all elements were made up of protons, electrons and  $\alpha$ -particles. The recent discovery of the neutron and positron has modified these conceptions and it is now believed that the main building units of complex nuclei are protons and neutrons. Since the  $\alpha$ -particle, presumably made up of 2 protons and

2 neutrons, is a very stable structure, it seems very probable that  $\alpha$ -particles exist as secondary units, but so far it has proved difficult to decide the relative number of these building units in different nuclei. It seems clear that the  $H^2$  isotope is made up of 1 proton and 1 neutron, the  $H^3$  isotope of 1 proton and 2 neutrons, and the  $He^3$  isotope of 2 protons and 1 neutron, but difficulties at once arise when we consider the structure of more complex nuclei. Is the lithium isotope of mass 7, for example, composed of 3 protons and 4 neutrons in an uncombined state or does it contain one  $\alpha$ -particle, one proton and 2 neutrons? Is the oxygen isotope of mass 16 made up of four  $\alpha$ -particles or does it contain protons and neutrons in an uncombined state? The evidence so far available is insufficient to give a definite answer.

Again, we are as yet uncertain of the relation if any between the proton and the neutron. It has been suggested that a conversion of one into the other may occur by the capture or loss of a negative or positive electron, and even that under some conditions negative protons may be formed. It is probable that an accurate determination of the magnetic moment or spin of the neutron and proton will be helpful in throwing further light on these important questions. It also seems clear that the spins of nuclei have to be taken into account in considering their structure and the types of transformation that may be possible. For this reason, it is highly important to know accurately the spins of all nuclei. Good progress has already been made in this direction by the application of direct optical methods.

When we consider the complexity of the structure of a heavy nucleus and the number of units that are condensed into its minute volume, it is obviously difficult to speak of the individual components as having a separate existence, for each constituent in a sense must occupy the whole nucleus. Bohr has pointed out that under such conditions, the theory of wave mechanics cannot be rigidly applied. Notwithstanding these difficulties and our uncertainty as to the detailed structure of nuclei, good progress has been made in several directions in interpreting in a general way some of the outstanding properties of nuclei. For example, Condon and Gurney and Gamow have given an explanation along broad lines of the spontaneous emission of  $\alpha$ -particles from the radioactive elements and an interpretation of the well-known Geiger-Nuttall relation. The theory of artificial disintegration worked out by Gamow has proved of great utility and is in general accord with the experimental facts although from the nature of the assumptions it must not be regarded

as more than a rough approximation. Again, Gamow has given a valuable interpretation of the fine structure of  $\alpha$ -rays and has obtained interesting information on the character of the energy levels in an excited nucleus. Heisenberg and Fermi have discussed the structure of atomic nuclei with special reference to the nature of the forces between proton and neutrons, while Fermi and Beck have worked out general theories to explain the mode of emission of  $\beta$ -particles from radioactive bodies. These important contributions will no doubt be a subject of much discussion at the Conference. Considering the great difficulties of the problem, excellent progress has been made by special assumptions with regard to the forces existing in the nucleus. At this stage of our knowledge, it is not to be expected that anything but tentative explanations can be given of the observed facts. A complete theory applicable to nuclei in general is probably far distant. The collection of experimental data is proceeding very rapidly and it may be that our theoretical ideas will have to be recast in view of possible new discoveries.

The development of our knowledge of nuclear physics is now at a most interesting and exciting stage and a close collaboration between the theoretical and experimental physicists is important for rapid progress in this most fundamental of problems.

# GENERAL QUANTUM THEORY





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# QUANTUM ELECTRODYNAMICS

By MAX BORN

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*ABSTRACT.* The paper is a short account of several publications by the author and L. Infeld, in which the idea of a unitary field theory is formulated. Instead of the different fields for all types of particles (electrons, protons, neutrons, neutrinos) there is assumed a single electromagnetic field which satisfies certain field equations which are modifications of Maxwell's equations. In these new equations the electric and magnetic field vectors are expressed in units of an absolute field, and they are invariant to general transformations.

The classical treatment leads to the existence of an electron with finite energy; it is possible to define a length, the radius of the electron, which has a definite numerical relation to the mass. The general solution of the two-dimensional electrostatic problem has been found by M. Pryce.

The quantum treatment is based on the assumption of commutation laws for the field components, considered as  $q$ -numbers. It is shown that a closed electromagnetic system behaves like a mass point satisfying the laws of quantum mechanics.

## § 1. INTRODUCTION

By the expression "quantum electrodynamics" I understand any attempt to formulate a theory describing simultaneously the behaviour of the electromagnetic field and the motion of all kinds of particles in conformity with the principles of quantum theory. It is well known that the existing theories meet very severe difficulties. I mention the result that a closed electrodynamic system has an infinite zero-point energy and that the electromagnetic energy of an electron (or any point charge) becomes infinite. But there are other very unsatisfactory points which seem to me still more important. I mean the increasing number of different kinds of fields: the Maxwell field of the photons, the Schrödinger or Dirac field of the electrons, the Fermi field of the neutrinos. For every kind of particle—electron, proton, neutron, neutrino—there has to be invented a separate kind of field, and all these fields have to be coupled by laws specially invented. The reason for this is the generally accepted dualistic idea corresponding to which the material particles are something essentially different from the electromagnetic field; they are assumed to be charged mass points, each with a characteristic mass constant. But charge means electromagnetic energy, and energy is equivalent to mass, in accordance with Einstein's fundamental equation  $E = mc^2$ . This electromagnetic mass becoming infinite for a point charge, has to be eliminated by some more or less artificial

assumption. Therefore all dualistic theories are in contradiction to Einstein's law, and this is the root of all difficulties. A way of avoiding these seems to me the introduction of a unitary theory which assumes only one kind of field, a modified electromagnetic Maxwell field the singularities of which play the rôle of particles.

## § 2. UNITARY THEORY: CLASSICAL TREATMENT

There have been several attempts to develop a unitary theory. All the older calculations of the electromagnetic mass of the electron are based on this idea; but they fail because they have to introduce arbitrary assumptions about the interior structure of the electron (for instance rigidity) or forces of non-electromagnetic origin to explain the cohesion of the electron, and this leads to a contradiction to Einstein's law. Mie made a more fundamental attempt: he tried to modify Maxwell's equations in such a way that electrons could exist as singularities of the field; but he introduced the absolute values of the potentials in the formulae, which is in contradiction to accepted physical facts. Then there are to be mentioned the theories started by Einstein who tried to connect the cohesive forces in the electron with gravitation: that these considerations did not succeed does not seem to me astonishing, because of the factor  $10^{40}$  which expresses the relative magnitude of electric and gravitational effects. I believe that all the unified field theories which tend to combine electromagnetism and gravitation into a single formalism are on the wrong track. Gravitation seems to be a small difference effect connected with the finiteness of the world and of the number of particles contained in it, and it should result from some high order approximation in the calculation of the interaction of the particles.

The unitary theory proposed by myself uses some of Mie's<sup>(1)</sup> formulae, but avoids the difficulties mentioned above. Maxwell's theory can be derived from a variation principle  $\delta \int L dx dy dz dt = 0$ , where  $L = \frac{1}{2} (\vec{E}^2 - \vec{H}^2)$ . The consideration that the field should never become infinite has led me to the assumption of a "maximum" or "absolute field," a constant  $b$ , and to the replacement of Maxwell's  $L$  by the function

$$L = b^2 \left( \sqrt{1 + \frac{1}{b^2} (\vec{B}^2 - \vec{E}^2)} - 1 \right) \quad \dots\dots(1).$$

Then Maxwell's field equations retain their form

$$\begin{aligned} \text{rot } \vec{H} - \frac{1}{c} \frac{\partial \vec{D}}{\partial t} &= 0, \quad \text{div } \vec{D} = 0, \quad \vec{D} = - \frac{\partial L}{\partial \vec{E}}, \\ \text{rot } \vec{E} + \frac{1}{c} \frac{\partial \vec{B}}{\partial t} &= 0, \quad \text{div } \vec{B} = 0, \quad \vec{H} = \frac{\partial L}{\partial \vec{B}} \end{aligned} \quad \dots(2),$$

but  $\vec{D}$ ,  $\vec{H}$ , are non-linear functions of  $\vec{B}$ ,  $\vec{E}$ .

Later Dr Infeld and I<sup>(2)</sup> found that this form of  $L$ , or rather a slightly more general one, can be derived from a very simple relativistic consideration. We assume that the metric and the electromagnetic field are the symmetric and antisymmetric parts

of a general tensor,  $a_{kl} = g_{kl} + f_{kl}$ ; ( $g_{kl} = g_{lk}$ ,  $f_{kl} = -f_{lk}$ ). Then the simplest variation principle for the  $f_{kl}$ , which is invariant and reduces to zero for  $f_{kl} = 0$ , is

$$\delta \int (\sqrt{-|g_{kl} + f_{kl}|} - \sqrt{-|g_{kl}|}) dx dy dz dt = 0 \quad \dots\dots(3),$$

where  $|a_{kl}|$  means the determinant of the tensor  $a_{kl}$ . Now, assuming  $g_{kl}$  in the normal form ( $g_{kl} = 0$  for  $k \neq l$ ,  $g_{11} = g_{22} = g_{33} = -1$ ,  $g_{44} = 1$ ) and using the usual notation ( $f_{23}, f_{31}, f_{12} \rightarrow \frac{\vec{B}}{b}$ ;  $f_{14}, f_{24}, f_{34} \rightarrow \frac{\vec{E}}{b}$ ), we obtain

$$\begin{aligned} -|g_{kl}| &= 1, \\ -|g_{kl} + f_{kl}| &= - \begin{vmatrix} -1, & \frac{1}{b} B_z, & -\frac{1}{b} B_y, & \frac{1}{b} E_x \\ -\frac{1}{b} B_z, & -1, & \frac{1}{b} B_x, & \frac{1}{b} E_y \\ \frac{1}{b} B_y, & -\frac{1}{b} B_x, & -1, & \frac{1}{b} E_z \\ -\frac{1}{b} E_x, & -\frac{1}{b} E_y, & -\frac{1}{b} E_z, & +1 \end{vmatrix} \\ &= 1 + \frac{1}{b^2} (\vec{B}^2 - \vec{E}^2) \end{aligned}$$

therefore

$$L = b^2 \left( \sqrt{1 + \frac{1}{b^2} (\vec{B}^2 - \vec{E}^2)} - \frac{1}{b^4} (\vec{B} \cdot \vec{E})^2 - 1 \right) \quad \dots\dots(4).$$

The additional term  $(\vec{B} \cdot \vec{E})^2$  vanishes for electrostatic fields ( $\vec{B} = 0$ ). The formula (3) and therefore the whole theory are generally invariant, without any restriction of the  $g_{kl}$ ; they determine the metric, but not the gravitational field. I believe that it is meaningless to introduce gravitation into the elementary laws of the field. For instance, it is not possible to split up a part of the force acting between two electrons and to call it gravitational attraction; but for bodies composed of many particles and neutral as a whole, this partition should be possible. This conviction induces me to neglect all considerations concerning gravitation. But I repeat that the theory is generally invariant.

From the field equations there follows the existence of a stress-energy-momentum tensor  $T_{kl}$  which satisfies divergence relations expressing the conservation laws of total momentum  $\vec{p}$  and energy  $W$  for a closed system. The 14, 24, 34 components of  $T_{kl}$  are the Poynting vector  $\vec{S}$ , the 44-component is the energy density  $U$ :

$$4\pi \vec{S} = \vec{D} \times \vec{B}, \quad 4\pi U = L + \vec{D} \cdot \vec{E} \quad \dots\dots(5),$$

and we have

$$\vec{p} = \int \vec{S} dv, \quad W = \int U dv, \quad dv = dx dy dz \quad \dots\dots(6).$$

But the conservation laws  $\vec{p} = 0$ ,  $\vec{W} = 0$  follow only if the field is regular. If singularities exist, this is not the case; but it is natural to postulate the conservation laws, and this postulate determines the motion of the singularities. Another equivalent way of obtaining the equations of motion of the singularities is to interpret the variation principle in such a way, that the integral has to be stationary not only for variations of the field for given singularities, but also for variations of the world lines of the singularities.

The simplest singularity possible is a point at rest surrounded by a central symmetrical field. In this case we have  $\vec{B} = \vec{H} = 0$ , and the field equations  $\text{div } \vec{D} = 0$ ,  $\text{rot } \vec{E} = 0$ , can be solved elementarily by

$$\vec{E} = -\text{grad } \phi, \quad \phi = \frac{e_0}{r} \int_{r_0}^{\infty} \frac{dx}{\sqrt{1+x^2}} \quad \dots\dots(7),$$

where  $e_0$  is an integration constant and  $r_0$  a distance, defined by  $b = \frac{e_0}{r_0^2}$ . The meaning of  $e_0$  is the charge;  $4\pi e_0 = \int \vec{D}_\nu ds \cdot r_0$  can be called the "electronic radius."  $\vec{D}$  becomes infinite at the centre, but  $\phi$ ,  $\vec{E}$  and the energy  $W_0$  are finite; the latter is

$$W_0 = m_0 c^2 = 1.2361 \quad \dots\dots(8);$$

the theory gives a definite numerical factor connecting rest-mass  $m_0$  and electronic radius  $r_0$ .

By transforming this solution to moving axes we see easily that Einstein's law  $W_0 = m_0 c^2$  is exactly satisfied. Infeld and I have proved by the variational method mentioned above that a closed system, for instance the electron, behaves in an external field like the Lorentz electron with a special distribution of "free" charge given by

$$4\pi\rho = \text{div } \vec{E} \quad \dots\dots(9).$$

Frenkel has obtained the same result by applying the conservation postulate directly. From this it follows that the classical laws of electronic theory hold as long as the electrons are at distances large compared with their radius  $r_0$ . The question of what may happen for electrons approaching one another closely is very difficult to answer because the differential equations are not linear. But we have succeeded in solving a simplified problem completely, the two-dimensional electrostatic case. The variation principle is then

$$\delta \int \sqrt{1 - \left(\frac{\partial\phi}{\partial x}\right)^2 - \left(\frac{\partial\phi}{\partial y}\right)^2} dx dy = 0 \quad \dots\dots(10),$$

and by substituting  $\phi = iz$  it goes over into the condition of minimum surface  $z(x, y)$ . This problem has been studied thoroughly by mathematicians. Weierstrass has solved the problem of representing all possible minimum surfaces giving

$x, y, z$  as functions of a parameter; but in geometry this solution is not very useful because the real difficulty consists in fitting the minimum surface into a given boundary curve. For our purpose this method gives everything wanted; for here the boundary conditions are: vanishing of  $\phi$  at infinity, and some singularities (points, lines, surfaces) in finite number. These conditions can be discussed by the method of complex functions. Mr M. Pryce<sup>(3)</sup> has worked out this method and found the following: There are solutions corresponding to any number of point charges of any size; but if there are more than one, the total force acting on one of them, expressed as the surface integral of Maxwell's stress tensor, does not vanish. Two or more charged points are not in static equilibrium, but must begin to move. (The law of this motion governed by the magnetic fields excited has not been found yet for small distances.) But there are other types of singularities; for instance, one where a finite part of a straight line is singular, the solution behaving like a classical dipole at great distance. For this type there seems to be no classical analogy. But we cannot decide whether it has a physical meaning (neutron?) before the corresponding problem has been solved for three dimensions and for moving singularities.

The force between two charges, as defined by the surface integral of the Maxwell stress-tensor, behaves like the classical force at large distances, but at very close distances it tends to a finite limit.

### § 3. FUNDAMENTAL FUNCTIONS AND TRANSFORMATIONS

The following considerations are a short report of a paper, written with Dr Infeld, which will shortly appear in *Proc. Roy. Soc.*\*

There exists a very close analogy between the formalism of our general electrodynamics and that of thermodynamics. It is well known that the thermodynamical laws for an isotropic substance can be expressed by fundamental functions in four different ways. There are two kinds of variables: mechanical variables—specific volume  $v$  and pressure  $p$ ; thermal variables—specific entropy  $s$  and temperature  $T$ . We can combine each variable of one kind with one of the others in four ways; each of these pairs can be considered as independent. To each pair there exists a fundamental function with the property, that the other pair can be found by simple differentiation of the fundamental function. We have the energy  $U(v, s)$ , the free energy  $F(v, T) = u - Ts$ , the heat function  $W(p, s) = U + pv$  and Gibbs potential  $Z(p, T) = U - Ts + pv$ ; the differentials are

$$\left. \begin{aligned} dU &= -pdv + Tds; & dF &= -pdv - sdT \\ dW &= vdp + Tds; & dZ &= vdp - sdT \end{aligned} \right\} \dots\dots(11).$$

In exactly the same way we can represent our electrodynamic laws in four different ways. Here we have two kinds of vectors, the electric vectors  $\vec{E}$ ,  $\vec{D}$  and the magnetic vectors  $\vec{B}$ ,  $\vec{H}$ ; we can combine one vector of each kind with one of the

\* The first part appeared in *Proc. Roy. Soc. A*, **147**, 522 (1934).

other in four different ways:  $(\vec{E}, \vec{B})$ ,  $(\vec{E}, \vec{H})$ ,  $(\vec{D}, \vec{B})$ ,  $(\vec{D}, \vec{H})$ . To each pair there belongs a fundamental function. The first  $L(\vec{E}, \vec{B})$  is the Lagrangian introduced above. Then we construct  $V(\vec{E}, U) = L - (\vec{H} \cdot \vec{B})$ ,  $U(\vec{D}, \vec{B}) = L + (\vec{E} \cdot \vec{D})$ ,  $H(\vec{D}, \vec{H}) = L + (\vec{E} \cdot \vec{D}) - (\vec{H} \cdot \vec{B})$  and have the differentials

$$\left. \begin{aligned} dL &= -\vec{D}d\vec{E} + \vec{H}d\vec{B}; & dV &= -\vec{D}d\vec{E} - \vec{B}d\vec{H} \\ dU &= \vec{E}d\vec{D} + \vec{H}d\vec{B}; & dH &= \vec{E}d\vec{D} - \vec{B}d\vec{H} \end{aligned} \right\} \dots\dots(12).$$

We immediately recognize  $U$  as the energy density defined in (5). The function  $H$  has been introduced in my first paper and called the Hamiltonian.  $V$  has not received a name yet and seems to be of no great interest. It can be objected against this procedure that the pairs  $\vec{E}, \vec{B}$  and  $\vec{D}, \vec{H}$  are antisymmetric tensors; the pairs  $\vec{E}, \vec{H}$  and  $\vec{D}, \vec{B}$  have not this property and do not obey simple transformation laws. This is the reason why in my first paper I have used only the functions  $L$  and  $H$ . But it has been found very convenient to give up the formal evidence of relativity invariance and to use especially the function  $U$ , because in quantum theory the notion of energy plays a central rôle: the invariance can be proved by a direct calculation. This state of affairs seems not to be very satisfactory, and it may be hoped that a method will be found of putting the invariance in evidence by the formalism itself.

So far everything holds for any function  $L(\vec{E}, \vec{B})$ . We introduce now the special function (4); but by choosing "natural units" we make  $b = 1$ . Then it is found by a little calculation that

$$4\pi U = \sqrt{1 + \vec{D}^2 + \vec{B}^2 + (4\pi\vec{S})^2} - 1 \quad \dots\dots(13),$$

where  $\vec{S}$  is the Poynting vector defined by (5). This formula has turned out to be the convenient starting point for formulating the quantum laws of the field.

#### § 4. QUANTUM THEORY OF THE FIELD

In my first paper I have tried to develop a new method of field quantization which is a direct analogue of Schrödinger's operator method; but the objects on which the operators act are not functions but functionals. Similar ideas have been worked out independently, and with greater mathematical skill, by W. H. Watson<sup>(4)</sup>. But none of these attempts was successful; present knowledge of functional calculus seems to be insufficiently developed for this purpose. In spite of my conviction that this way will at last lead to the result wanted, we have preferred<sup>(5)</sup> to try first the method used by other investigators in this field, postulating commutation laws for the field components. From the considerations of Heisenberg and Pauli it follows that these relations connect the vectors  $\vec{D}$  and  $\vec{B}$ ; we write them here in natural

units ( $c = 1$ ;  $e_0 = 1$ ;  $b = 1$ , therefore  $h = 137$ ,  $1 = \frac{2}{\alpha}$  where  $\alpha$  is the fine structure constant):

$$[B_k, \bar{B}_i] = [D_k, \bar{D}_i] = 0, \quad [D_k, B_k] = [B_k, \bar{D}_k] = 0 \quad \dots\dots(14),$$

$$[D_1, \bar{B}_2] = -[B_1, \bar{D}_2] = 4\pi \frac{\partial}{\partial z} \delta(r - \bar{r}),$$

where

$$i\alpha [D_1, \bar{B}_2] = (D_1 \bar{B}_2 - \bar{B}_2 D_1), \text{ etc.}$$

Here the components  $B_k$ ,  $D_k$  of  $\vec{B}$ ,  $\vec{D}$  are considered as  $q$ -numbers, which are functions of the  $c$  numbers ( $x, y, z, t$ ).  $r$  represents the point  $x, y, z$ , and  $\bar{r}$  the point  $\bar{x}, \bar{y}, \bar{z}$ , and  $\bar{B}_1$  means  $B_1(\bar{x}, \bar{y}, \bar{z}, t)$ , etc.  $\delta$  is the product of three Dirac functions

$$\delta(r - \bar{r}) = \delta(x - \bar{x}) \delta(y - \bar{y}) \delta(z - \bar{z}) \quad \dots\dots(15).$$

The relations (14) can be considered as established by a careful investigation of Bohr, who has shown that they lead to exactly the same uncertainty laws for measuring field strengths as can be derived by a direct application of the definition of the field as giving the forces acting on electrons. The invariance of the relations (14) with respect to Lorentz transformations is not immediately obvious, but can be shown by the method of infinitesimal transformation with the

help of a direct calculation. The functions of  $\vec{B}$ ,  $\vec{D}$  appearing in the theory explained above have now to be replaced by functions of  $q$ -numbers, but these are in general not uniquely determined, in consequence of the non-commutativity. We proceed in the same way as in usual quantum mechanics, symmetrizing products; e.g. the Poynting vector has to be defined instead of (5) by

$$4\pi \vec{S} = \frac{1}{2} [(\dot{\vec{D}} \times \vec{B}) - (\vec{B} \times \dot{\vec{D}})] \quad \dots\dots(16),$$

which is identical with the original definition when  $\vec{B}$  and  $\vec{D}$  are  $c$  numbers. The most important point of this theory is now that it is not necessary to add the complete set of Maxwell's equations as independent suppositions (like the older theories do), but only the divergence equations

$$\text{div } \vec{D} = 0, \quad \text{div } \vec{B} = 0 \quad \dots\dots(17).$$

We consider now a closed system, i.e. one for which the field components vanish at infinity quickly enough for all surface integrals expressing external actions to be neglected. For such a closed system the time-derivative can be defined by the commutation with the total energy

$$\frac{\partial F}{\partial t} = i\alpha (WF - FW) = [W, F] \quad (18),$$

for any function  $F(\vec{D}, \vec{B})$ ; then all the other Maxwell equations (2) are a consequence of the commutation laws (14). Moreover, with the help of (14) and (17) it follows easily that

$$-\frac{\partial F}{\partial x} = i\alpha (p_x F - F p_x) = [p_x, F] \quad \dots\dots(19),$$



where  $\vec{p}$  is the total momentum (6). Therefore, Maxwell's equations can be written entirely with the help of commutation brackets.

We can now show that a closed system as a whole behaves like a system obeying the usual laws of quantum mechanics. For this purpose we define the *energetic centre* as follows:

$$q_w = \frac{1}{2} [W^{-1} (\int x U dv) + (\int x U dv) W^{-1}] \quad \dots\dots(20).$$

Then it can be shown that

$$[p_k, q_k] = i\alpha (p_k q_k - q_k p_k) = 1; \quad [p_k, q_l] = 0 \quad (k \neq l) \quad \dots\dots(21).$$

We have, of course,

$$[W, \vec{p}] = 0 \quad \dots\dots(22),$$

but

$$\vec{q} = i\alpha (W\vec{q} - \vec{q}W) = [W, \vec{q}] = pW^{-1} \quad \dots\dots(23),$$

whence

$$[W, \vec{q}] = \vec{q} = 0 \quad \dots\dots(24).$$

The system as a whole moves uniformly in a straight line. From the definition (13) of  $U$  it follows that the 4-vector  $\vec{p}$ ,  $W$  has time-character or is a zero-vector:

$$W^2 - \vec{p}^2 \geq 0.$$

Therefore we can put

$$W^2 - \vec{p}^2 = m_0^2 \quad \dots\dots(25),$$

and can consider  $m_0$  as the  $q$ -number representing the total rest-mass of the system. The formulae (21) to (25) show that the energetic centre of the systems obeys the laws of relativistic quantum mechanics of a free particle without regard to the spin. If the field can be split up into two parts, the inner field and the external field, and if the latter is weak and can be treated as a  $c$ -number field, it can be shown that (25) has to be replaced by the Gordon-Klein equation

$$(W - e\phi)^2 - (\vec{p} - e\vec{a})^2 = m_0^2 \quad \dots\dots(26),$$

where  $\phi$ ,  $\vec{a}$  are the scalar and vector potentials of the external field and  $e$  the total charge, defined by

$$e = \int \rho dv = \frac{1}{4\pi} \int \text{div } \vec{E} dv \quad \dots\dots(27).$$

It is very important that it can be shown that the total angular momentum of the system

$$\vec{M} = \int (\vec{r} \times \vec{S}) dv$$

has all the properties known from quantum mechanics. For we find\*

$$\left. \begin{aligned} [M_x, p_x] &= 0; & [M_x, p_y] &= -p_z, \dots \\ [M_x, q_x] &= 0; & [M_x, q_y] &= -q_z, \dots \end{aligned} \right\} \quad \dots\dots(28),$$

and

$$[M_x, M_x] = 0, \quad [M_x, M_y] = -M_z \quad \dots\dots(29).$$

From the relations (29) it follows immediately in a well-known manner that

\* See addendum opposite.

one component of  $\alpha\vec{M}$ , say  $\alpha M_z$ , has eigenvalues either  $\pm 1, \pm 2, \dots$  or  $\pm \frac{1}{2}, \pm \frac{3}{2}, \dots$  and that  $\alpha^2 \vec{M}^2 = j(j+1)$ , where correspondingly  $j = 1, 2, \dots$  or  $j = \frac{1}{2}, \frac{3}{2}, \dots$  and  $|M_z| \leq j$ .

We prove easily that the quantities  $\vec{M}, \vec{p}, W$  obey the conservation laws, i.e.

$$[W, \vec{M}] = \vec{M} = 0; \quad [W, \vec{p}] = \vec{p} = 0; \quad [W, W] = \dot{W} = 0.$$

In quantum mechanics we have the theorem: If we have a system of quantities ( $q$ -numbers or matrices) and if we have an expression  $\beta$  which commutes with all quantities of our system, then we can regard  $\beta$  in all considerations in which only the quantities of our system are involved, as a  $c$ -number. We can apply this criterion to the system of quantities which characterize the whole field, i.e. to

$$\vec{M}, \vec{p}, q, W \quad \dots\dots(30).$$

It can be shown that the square of the rest-mass

$$m_0^2 = W^2 - \vec{p}^2 \quad \dots\dots(31),$$

commutes with all expressions in (30) and can, therefore, be regarded as a  $c$  number.

Our theory would be complete if we could show that the total charge is necessarily an integer (in our natural units); but this result we have not yet obtained. Then the investigation of the possible values of  $m_0$  for irreversible systems or particles would be of the greatest interest, with regard to the question whether this theory is able to explain not only the existence of the electron, but also of the proton, neutron and other particles.

The determination of the smallest value of  $e$ , or the elementary electric charge, is equivalent to a theoretical calculation of the fine structure constant  $\alpha$ , the central problem of atomic physics. The success or failure in this point will be decisive for the validity of the theory.

#### *Addendum, December 1934.*

We have since found that the coordinates  $q_x, q_y, q_z$  do not commute. This fact is obviously connected with the existence of the spin, as we shall show in Part 2 of the paper quoted in (5).

#### REFERENCES

- (1) M. BORN. *Proc. Roy. Soc. A*, **143**, 410 (1933).
- (2) M. BORN and L. INFELD. *Proc. Roy. Soc. A*, **144** (1934).
- (3) M. H. L. PRYCE. *Proc. Camb. Phil. Soc. (in the press)*.
- (4) W. H. WATSON. *Trans. Roy. Soc. of Canada, Ser. III*. **28** (1934).
- (5) M. BORN and L. INFELD. *Proc. Roy. Soc. A*, **147**, 522 (1934).



# NATURAL $\beta$ -DECAY



# REPORT ON THEORETICAL CONSIDERATIONS CONCERNING RADIOACTIVE $\beta$ -DECAY

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**ABSTRACT.** The fact that the  $\beta$ -particles emitted by radioactive bodies are not homogeneous, but give a continuous spectrum, cannot be reconciled with what is known from  $\alpha$ -disintegration and other sources as regards the quantized states of nuclei, unless the assumption is made that a second particle, other than the observed electron, is emitted in such processes.

The hypothesis which has been proposed by Pauli is that this particle is a neutrino (an unobserved particle with small mass, no charge, and spin  $\frac{1}{2} \frac{h}{2\pi}$ ). Whatever the particle, such a hypothesis accounts for the fact that the  $\beta$ -ray energy spectrum has a finite upper limit, which will be reached on those occasions when the second particle has very little or no energy.

An alternative hypothesis developed in this paper is that the second particle is a positive or negative electron, which is subsequently captured by the nucleus, following laws not yet known.

With the most primitive form of these hypotheses, the angular momentum would be distributed in a statistical manner, like the energy, and it is shown that this leads to the prediction that negative electrons of small energy would be freely emitted; to avoid this, it is necessary to introduce a special selection rule. Some justification for this is found in the assignment to groups of free nuclear charges of a quantum number  $j$ , which must not however be held to have the same definite mechanical interpretation inside the nucleus as it has outside.

The theory fits in well with a number of observed facts, such as the Sargent curves, and the order of magnitude of the decay constants.

## § 1. INTRODUCTION

THE progress of the investigation on radioactive phenomena led quite early to the conclusion that the transformation of several radioactive elements is due to the emission of an electron by the atomic nucleus. This process increases the charge of the nucleus by one elementary unit and changes its mass only within the limits of the order of the mass defects.

We may regard the magnitude of the energies involved in these processes and the average life periods which are attributed to the radioactive  $\beta$ -bodies as the characteristic features of  $\beta$ -emission. The decay energies are of the order

$$\Delta E \sim mc^2 = 0.5 \cdot 10^6 \text{ e.V.} \quad \dots\dots(1),$$

which is just about the rest energy of an electron. The average life periods  $\tau$  which are connected with the rate of decay  $\lambda$  by

$$\tau = \frac{1}{\lambda}$$

have been found to be of the order of several minutes or hours. These are macroscopic time periods, very large compared with the time intervals which we are accustomed to see involved in atomic phenomena, but still very small compared with the duration of geological epochs.

The  $\beta$ -emission will be connected later on with the creation of an electron which naturally requires a minimum energy of the order (1), and this will lead us to an understanding of the magnitude of the decay energies. No such understanding, however, can be obtained at present of the observed magnitude of the decay constants, the phenomena coming into play here lying beyond the reach of the present theory.

It follows from the magnitude of the decay constants that the spontaneous occurrence of  $\beta$ -emission can only be detected in a few cases, when the  $\beta$ -body is a derivative of a substance with an average lifetime comparable with geological periods. This condition is well known to be fulfilled in the case of heavy radioactive elements only. There can be, however, no doubt that the  $\beta$ -emission is a very general phenomenon characteristic of most of the nuclear aggregates. This has only recently been shown in a very convincing way by Curie and Joliot when they found a number of artificially produced light isotopes to be  $\beta$ -active, emitting either positive or negative electrons.

It has to be noticed, however, that beside the  $\beta$ -emission considered above, there seems to exist a second type of  $\beta$ -activity of extremely long half-period. This phenomenon has been detected in potassium and rubidium, but so far it has not yet been investigated very closely. The very weak activity of these elements will not be included in the following discussion.

## § 2. THE CONTINUOUS $\beta$ -SPECTRA

The theoretical discussion on  $\beta$ -emission was initiated by Bohr, who has drawn attention to the amazing fact that the  $\beta$ -electrons are not homogeneous as are, for instance, the radioactive  $\alpha$ -particles, but leave the nucleus with an energy distribution varying between wide limits.

The continuous  $\beta$ -spectra have been carefully examined by Ellis and others. Especially in the case of Ra E it has been possible to show that no energy loss other than by the  $\beta$ -emission can be observed by present means. The first and most natural interpretation of this fact seemed to be the assumption that the energy of a nucleus involved in a  $\beta$ -transformation was not quantized but varied continuously between the limits indicated by the  $\beta$ -spectra. This behaviour would, however, be in contradiction with what we know about the well-defined energies of the nuclear  $\alpha$ - and  $\gamma$ -rays, and Bohr has shown that it would also scarcely be reconcilable with the experiments on molecular spectra which clearly show that two nuclei of the same kind behave as identical particles. In the same way we have to conclude from the hyperfine structure of the atomic spectra that a nucleus must be regarded as a quantized system of well-defined angular momentum.

Assuming now that every nucleus is in a well-defined energy state, the  $\beta$ -emission will in every case set free an amount of energy, say  $\Delta E$ , which in general will be

different from the energy  $W$  of the emitted electron. The question arises: What happens to the energy difference  $\Delta E - W$ , an equivalent for which has not been detected in experiments to date?

We are faced with the same difficulty as to the energy if we consider the spin (angular momentum) or the statistical character of the electrons assumed to be present in a nucleus. Certain paradoxes revealed by experiments on the determination of nuclear momenta and statistics indicate that an electron entering the nucleus loses its angular momentum as well as its statistical properties, in brief, every one of its mechanical quantities which we should expect to obey a conservation law.

These difficulties, arising from the discussion of the experimental evidence, seem to be of a somewhat serious character; the situation, however, grows even worse if we consider the present state of the theory concerned with the phenomena in question. The Dirac theory of the electron fails to account for a stable binding of an electron within nuclear dimensions. It has been pointed out by Bohr that the failure of this theory is due to the incompleteness of its fundamental assumptions. Taking into account more exactly the essential coupling between the electron and the surrounding electromagnetic field we should be led to entirely new results when the dimensions of the system considered become comparable with the so-called radius of the electron

$$a = \frac{e^2}{mc^2} = 2.81 \cdot 10^{-13} \text{ cm.},$$

which is of the order of the nuclear dimensions.

As the phenomena considered here lie beyond the reach of the wave-mechanical treatment, Bohr has expressed the view that the difficulties discussed above might possibly be due to the failure of the mechanical conservation laws<sup>(1)</sup>.

### § 3. THE "NEUTRINO" HYPOTHESIS

The paradoxes concerning the mechanical integrals of motion involved in the  $\beta$ -emission process can be described in the following way:

Let  $A$  be a mechanical quantity for which a conservation law is expected to hold, and  $\Delta A$  the difference of the respective quantities referring to the initial and final states of the nucleus being transmuted by  $\beta$ -decay. Then we can write

$$\Delta A = A + A' \quad \dots\dots(2),$$

where  $A$  belongs to the—positive or negative—electron emitted and  $A'$  represents the quantity apparently lost for which no equivalent has been found in experiments. If in particular  $A$  is understood to be the energy, (2) becomes

$$\Delta E = W + W' \quad \dots\dots(3).$$

(2) and (3) can now formally be interpreted by ascribing the quantities  $A'$  to an unknown new particle which is assumed to be emitted simultaneously with the  $\beta$ -particle and which eventually becomes lost after the emission process. This interpretation is supported by the fact that the continuous  $\beta$ -spectra have a finite upper



energy limit, and that in consequence of this  $W'$  in (3) never takes negative values. If  $m'$  denotes the mass of the hypothetically introduced new particle we conclude easily from (3) that the  $\beta$ -emission is subject to the energy condition

$$\Delta E > (m + m') \cdot c^2 \quad \dots\dots(4).$$

Considering the determinations of the mass of the heavy elements it is very unlikely that  $m'$  would take too high values, and thus (4) is in agreement with (1).

The fundamental equation (3) can be checked with the experimental data available for the radioactive branches. A radioactive branch transition consists in an alternative emission of either an  $\alpha$ - and a  $\beta$ -particle ( $CC''D$  transition) or first a  $\beta$ - and then an  $\alpha$ -particle ( $CC'D$  transition), both of which lead to the same end-product. Though the energies actually emitted on both sides of the branch will be different in general we should expect according to (3) that the same value would be obtained by adding to the energy of the  $\alpha$ -emission the upper energy limit of the continuous  $\beta$ -spectrum. This has been found to agree with the experimental data by Ellis and Mott<sup>(2)</sup> and by the author<sup>(3)</sup>. Though the data available at present are not yet very exact it seems very likely that the relation (3) is correct.

Pauli has observed that it would not be in contradiction with experiment to ascribe a real existence to the particle formally introduced, and it has been proposed to call this particle a "neutrino." This neutrino must be regarded as a neutral particle of small mass with an angular spin momentum of  $\frac{1}{2} \frac{h}{2\pi}$  and obeying the Fermi statistics. Such a particle would indeed be very difficult to detect owing to its extremely high penetrating power. Chadwick has been searching for the ionization due to a neutrino radiation eventually emerging from a radioactive  $\beta$ -body, but no indication of such ionization could be found. We may conclude from Chadwick's measurements that a neutrino—if it exists at all—has a magnetic moment small compared with  $\frac{e}{2m'c} \frac{h^{(4)}}{2\pi}$ .

The very reason for the introduction of the neutrino hypothesis was to maintain the validity of the conservation laws also for nuclear processes. We have seen, however, that it is not possible at present to find general theoretical arguments whether or not the conservation laws should apply within dimensions of the order of the radius of the electron. It must be noticed that the assumption of the real existence of a neutrino will scarcely be helpful in removing the main difficulty of the present theory, i.e. in accounting for the nuclear stability. If a neutrino should be proved to exist this would undoubtedly mean a considerable complication for the theory and would give rise to new difficulties. There is only very little hope of including the neutrino in the general theory of the electron or of the electromagnetic field. Treating, however, the neutrino as a new elementary particle, we should at once be confronted with the well-known difficulty of the states of negative energy which has only recently been removed for the electron. Thus we should have to assume beside the neutrino also an "antineutrino." It must be said, however, that a direct experimental proof of the non-existence of a neutrino can never be found.

Whatever the accuracy obtained might be, it would be possible to provide the neutrino with properties enabling it to escape observation.

Thus the question whether a neutrino exists or not must at present remain undecided, but we shall see later on that this question is less important for the treatment of the  $\beta$ -decay than one would think at first. Whatever the solution of this question may be, we have to expect that phenomena connected with the "production of a neutrino" will always be essentially limited to small dimensions of the order  $a = \frac{e^2}{mc^2}$ , and will not occur in dimensions comparable with the Compton wavelength.

#### § 4. THE DECAY FORMULA

In order to proceed on the details of the  $\beta$ -transformation, it will be found advantageous to make use of some general properties of the wave emission by a small source which we shall first derive here.

We consider a source the dimensions of which may be very small compared with the wave-length of the emitted radiation. To a first approximation this source may be regarded as a point. The emission of a particle can then be treated as an excitation, in the neighbourhood of the source, of an eigenfunction belonging to the continuous spectrum of the wave equation. The probability of the emission of a particle with energy  $W$  will evidently be proportional to the density of the eigenfunctions in the energy interval in question. This density function may be written  $D(W)$  and must naturally be taken at the point of the source. Thus we obtain for the emission probability or decay constant

$$\lambda = k \cdot D(W) \quad \dots\dots(5),$$

the coefficient  $k$  depending on the special properties of the model of the source and being a slowly varying function of  $W$ . The formula (5) has been derived only from the geometrical arrangement characteristic of every wave emission, and must therefore be expected to hold for any special model of the source. It can, however, include no information about the details of the coupling between the source and the emitted radiation. It is, indeed, easy to see that (5) leads to the well-known formulae for the emission of electromagnetic dipole, quadripole, etc., radiation if we introduce for  $D(W)$  the values resulting from Maxwell's equations, and Gamow's formula for the radioactive  $\alpha$ -decay if  $D(W)$  is understood to be the Schrödinger density function in a repulsive Coulomb field<sup>(5)</sup>.

In order to apply (5) to the  $\beta$ -emission process, we must remember that the  $\beta$ -decay must be formally treated as a double process. The probability of an emission in the energy interval between  $W$  and  $W + dW$  may be called  $\mathcal{J}(W) \cdot dW$ . Then we obtain similarly to (5)

$$\mathcal{J}(W) = k \cdot D_1(W) \times D_2(W') \quad \dots\dots(6),$$

where  $W$  and  $W'$  are connected by (3). The symbolic multiplication  $\times$  is only to indicate that in the case of Dirac's theory the product of the density functions has to be replaced by the square of a spinor product. Evidently (6) and (3) describe a

continuous spectrum varying between the limits  $W = mc^2$  and  $W = \Delta E - m'c^2$  and we get finally for the total decay constant

$$\lambda = \int_{mc^2}^{\Delta E - m'c^2} \mathcal{F}(W) \cdot dW \quad \dots\dots(7).$$

$D(W)$  in (5) and (6) are monotonically increasing functions of the argument. (6) describes therefore an intensity distribution of the continuous  $\beta$ -spectrum showing a maximum between the limits. The observed shape of the  $\beta$ -spectra is just of the type (6). It will now be our task to determine the correct functions  $D_1$  and  $D_2$  in order to represent the empirical curves.

### § 5. THE SHAPE OF THE $\beta$ -SPECTRUM

As far as the choice of  $D_1$  is concerned, no ambiguity can arise. This function evidently corresponds to the particles emitted by the nucleus, and thus will be given by Dirac's density function for a positive or negative electron in the Coulomb field surrounding the nucleus.

We can see from (6) that  $D_1$  mainly influences the shape of the  $\beta$ -spectrum in the neighbourhood of the lower limit, that is, for small energies of the emitted  $\beta$ -particles. The density function itself depends on the angular momentum quantum number  $j$  of the electron to be emitted, and we have therefore first to consider the angular momenta coming into play.

Applying (2) to the angular momentum balance, we find that the angular momentum furnished by the nucleus fixes only the sum of the angular momenta of the two particles taken into account but not that of one single particle. Thus we should expect at first that, in every process, electrons of any angular momentum would be emitted. This behaviour would exactly correspond to what we know about the energy.  $D_1$  decreasing rapidly with increasing quantum number, we should be led to assume that mainly electrons with  $j = -1$  ( $s_{\frac{1}{2}}$ -electrons) would occur. In this case we should have to conclude from (6) that there is, as a rule, a considerable probability of the emission of a negative electron of small energy. This conclusion, however, is in contradiction with the experimental data.

It may be noticed that our argument can be applied to the emission of negative electrons only. If  $D_1$  corresponds to a positively charged particle it will in every case tend to zero with an exponential factor of the Gamow type if  $W$  decreases, and thus no qualitative disagreement would arise in this approximation.

In order to reconcile (6) with the experimental data, the introduction of a new assumption seems to be indispensable. This assumption must evidently operate to exclude the emission by some elements of  $s_{\frac{1}{2}}$ - and in the case of Ra E even of  $p_{\frac{3}{2}}$ -electrons. No definite result has so far been obtained on this additional assumption, but we shall see later on that it is reasonable to establish a selection rule permitting only one well-defined value of the angular momentum in every transition. We shall also have to discuss the reasons why, in this respect, the angular momentum should be treated differently from the energy.

$D_2$  corresponds to the formally introduced second particle, and is responsible for the shape of the  $\beta$ -spectrum in the neighbourhood of the upper energy limit. The formal properties of this particle being unknown to a large extent, it will be found rather difficult to determine its correct density function. If we assume  $m'$  to be comparable with the electronic mass  $m$ , we find here exactly the same difficulty as above for the lower energy limit. This difficulty, however, will be removed simultaneously with the first one by the selection rule to be established for the angular momentum.

Though no definite statement can be obtained at present with regard to  $D_2$  it is seen from (6) that the discussion of the shape of the continuous  $\beta$ -spectrum opens up a promising way to investigate the properties of the unknown formally introduced particle or neutrino.

#### § 6. $\beta$ -EMISSION AND NUCLEAR STRUCTURE

So far our developments have mainly been based on experimental facts. They are common to the theory first given by Sitte and the author<sup>(6)</sup> as well as to the treatment of the  $\beta$ -decay proposed somewhat later by Fermi<sup>(7)</sup>. If we want, however, to obtain a more complete picture of the  $\beta$ -decay process and to connect the features of the  $\beta$ -emission with the details of the nuclear structure, a somewhat more speculative procedure must be followed. Different views have been taken in this respect by several authors.

Fermi has tried to connect the  $\beta$ -emission process with some views expressed previously by Heisenberg<sup>(8)</sup>. According to these a nucleus should be built up of protons and neutrons only. A  $\beta$ -transformation would then consist of an intranuclear transition from a neutron to a proton or from a proton to a neutron. Taking this for granted the  $\beta$ -emission would only depend on the properties of the two assumed elementary particles and on the type of their motion inside the nucleus.

Fermi lays much emphasis on the fact that a fairly satisfactory formal connexion between Heisenberg's theory and the treatment of the  $\beta$ -decay can be established. We must remember, however, that the general character of the  $\beta$ -emission is mainly determined by the geometrical conditions of wave emission and thus supplies us with no additional evidence in favour of Heisenberg's assumptions. Heisenberg's theory undoubtedly accounts for the well-defined nuclear quantum states and contains some interesting suggestions on the relation between protons and neutrons. Nevertheless, it is exposed to some serious objections which make it doubtful whether an attack on these lines can be successful.

The first difficulty of Heisenberg's theory arises from energy considerations. The energy involved in a proton-neutron transition is known to be of the order of a few times  $mc^2$ ; the energies to be attributed to the heavy particles, however, are at least of the order  $10mc^2$ . It is difficult to see why in a nucleus, for instance, an  $\alpha$ -particle with binding energy of 27 millions e.V. should be regarded as less stable than a neutron or a proton.

Recent investigations by Curie and Joliot<sup>(9)</sup> have suggested that the mass of the

neutron is considerably higher than that of the proton. This view is supported by the high mass of the  $\text{Be}_9$ -nucleus. The condition (4) being satisfied, the possibility still cannot be excluded that the neutron is an unstable aggregate, and that it might be found to be  $\beta$ -active in the same way as the other recently detected isotopes. Owing to the extremely long life-periods of  $\beta$ -transitions, this would not in principle preclude a decomposition of any nucleus into protons and neutrons, but even this would not mean that inside the nucleus individual protons and neutrons must exist. It would scarcely be possible to prove that the particles of small binding energy ultimately resulting have not been produced only by the decomposition process itself.

Another objection arises from the fact that in Heisenberg's and Fermi's formalism an intranuclear electron is accounted for with only one degree of freedom. It seems rather difficult to imagine how a continuous process such as the production and emission of a Dirac electron by a nucleus could be represented in this rough way.

## § 7. THE THEORY OF FERMI

Thus the special assumptions about the details of the nuclear structure seem still to be of a rather hypothetical character. The main results about the  $\beta$ -decay, however, do not depend on these assumptions, and we will try to discuss Fermi's theory from a more general point of view.

Fermi considers the particle which we have formally introduced in § 3 as a neutrino having a real existence. He identifies the wave equation of this particle in a somewhat arbitrary way with Dirac's equation for an electron in free space and thus obtains immediately a definite expression for the density function  $D_2$  in (6). Then Fermi considers the mass  $m'$  of the neutrino as an arbitrary parameter, and he finds that (6) fits qualitatively the empirical curves in the neighbourhood of the upper energy limit if  $m' = 0$ .

Introducing (6) in (7) we can determine the dependence of the rate of decay on the upper energy limit  $\Delta E$  of the  $\beta$ -spectrum. (7) has been found to agree qualitatively with the experimental data for a number of  $\beta$ -bodies. There exists, however, a second group of  $\beta$ -active elements the rates of decay of which are several hundred times smaller than one would expect from (7)<sup>(10)</sup>. Fermi believes that this second group of  $\beta$ -bodies can be explained if we assume that the nucleus changes its angular momentum in these transitions\*. This would correspond to what we know about dipole and quadripole transitions in the case of electromagnetic radiation.

Fermi's assumptions, however, seem to be insufficient to remove the difficulties already mentioned in § 5 which concern the shape of the  $\beta$ -spectrum near the lower energy limit. The curves obtained from Fermi's formulae give as a rule too high values for the emission probability of slow negative electrons. Most of the measurements, however, are still rather rough and the conclusions drawn from them are perhaps not yet quite definite.

More complete data are available at present only for Ra E. Miss Meitner has investigated the distribution in the continuous  $\beta$ -spectrum of this element and she

\* Cf. Dr Sitte's remarks on this point, p. 68.

finds that practically no electrons are emitted with energy below 50,000 e.V. Although in Fermi's formulae the number of slow electrons is somewhat reduced if a change of nuclear angular momentum takes place during the  $\beta$ -transformation, yet Meitner's result still seems to be incompatible with Fermi's theory\*.

### § 8. SYMMETRY CONSIDERATIONS

Another attempt to give an interpretation of the general formalism of §§3 and 4, which so far seems to avoid the difficulties discussed above, has been made by Dr Sitte and the author<sup>(6)</sup>.

If we start from the given energy conditions we must assume that a nucleus contains as a rule as many  $\alpha$ -particles as is compatible with its mass. Then the heavier nuclei must contain, beside the  $\alpha$ -particles, a certain number of "free" nuclear charges. Plotting the number of free charges against the assumed number of  $\alpha$ -particles we find a simple regularity. The free nuclear charges occur in groups of a certain multiplicity which is similar to the term multiplicity in the atom.

In Dirac's theory the multiplicity of a term is a direct consequence of the spatial symmetry properties of the Dirac electron. In a central field the multiplicity of a term is given by  $2 \cdot |j|$ , if  $j$  denotes a quantum number characteristic for the order of the spherical harmonics involved. Thus we can formally ascribe a quantum number  $j$  to every group of free nuclear charges<sup>(12)</sup>.

In the quantum theory of the atom, the quantum number  $j$  has also a mechanical meaning and determines the angular momentum of the quantum state in question,

$$\gamma = \frac{h}{2\pi} \cdot \sqrt{j^2 - \frac{1}{4}}.$$

It is doubtful, however, whether this mechanical interpretation of  $j$  can be maintained inside the nucleus. As we have seen in §2 any mechanical concept which essentially involves the dimension of a length may fail within a region comparable with the radius of the electron  $\frac{e^2}{mc^2}$ .

No reason, however, can be found for expecting a failure of those concepts which do not include the dimension of a length and therefore do not depend upon the radius of the electron. This argument holds in particular for all symmetry considerations. It is conceivable that an electron may retain its symmetry properties inside the nucleus and thus the use of a quantum number  $j$  for nuclear charges may be justified as long as we do not attach to it a mechanical meaning.

The  $\beta$ -transformation of the heavy radioactive elements consists in the emission of free nuclear charges which become unstable after a reduction of the number of  $\alpha$ -particles by  $\alpha$ -decay. If our view is correct we should expect that in every  $\beta$ -

\* We have evaluated several of Fermi's integrals and have found that even a very large change of angular momentum would not be sufficient to explain Miss Meitner's results. This change of angular momentum, moreover, would reduce the rate of decay (7) to too small a value. Our calculations have led in several points to results different from what has been estimated in Fermi's paper<sup>(11)</sup>. We have, however, not yet been able to settle these questions with Prof. Fermi.

transition an electron of definite quantum number  $j$  would come into play. This is just the selection rule which we have found to be required in § 5. This rule, however, does not refer directly to the angular momenta of the particles concerned but to their symmetry properties. Owing to the close connexion between symmetry and mechanical quantities which holds outside the nucleus, our selection rule leads nevertheless indirectly to a selection of angular momenta by the nucleus. We can see at once that no similar symmetry relation corresponds to the energy. This may be the reason why in some respects energy and angular momentum behave differently. According to (2) the conservation laws of both of these quantities are violated during the  $\beta$ -decay; the energy loss  $W'$  varies between wide limits, the loss of angular momentum  $\mathcal{J}'$ , however, is a well-defined quantity.

Since a heavy nucleus can contain as many as twenty-six free nuclear charges, we must be prepared to find fairly high values for our quantum number.  $|j|$  will be found later on to assume the values 2 and 3 corresponding to the angular momenta  $\frac{3}{2} \frac{h}{2\pi}$  and  $\frac{5}{2} \frac{h}{2\pi}$ . It may be noticed that never more than four  $p_{\frac{1}{2}}$ -electrons will be emitted by one radioactive family. This is what we have to expect from our point of view.

#### § 9. TREATMENT OF THE $\beta$ -DECAY

We have seen in §§ 3 and 4 that a second particle of hypothetical character occurs during the production of a  $\beta$ -electron. Until recently it has not been possible to find in Dirac's theory of the electron an indication of a double process of the type of (6). The development of the theory of the positive electron, however, has revealed that two particles are involved in every production of an electron. Therefore, if we wish to retain Dirac's theory as far as possible, it seems more reasonable to connect (6) with the well-known production of a pair of differently charged particles than to assume an entirely new particle of the type of a neutrino. We shall see later on that our procedure is necessary for a subsequent application of our selection rule for the angular momenta.

If now we interpret (6) as the production of a pair of differently charged electrons, no ambiguity remains in the choice of  $D_2$  and we immediately obtain  $m' = m$ . Thus the condition (4) for the occurrence of a  $\beta$ -transformation becomes

$$\Delta E > 2mc^2 \quad \dots\dots(8),$$

and the symmetrical form of (6) applies both to the emission of positive and negative electrons. From this point of view (6) has been applied in detail to the treatment of the  $\beta$ -decay by Dr Sitte.

We have at least to discuss what happens to the second particle in (6) which here is formally treated as a positive or negative electron. Since we know that the nucleus changes its charge by one unit during the  $\beta$ -transformation, we must assume the charge of the second electron to be captured by the nucleus in a way lying beyond the reach of Dirac's theory. As has been discussed above, the particle must in this absorption process lose all its mechanical quantities  $\mathcal{A}'$  from equation (2), but it may retain its symmetry properties.

The treatment of the  $\beta$ -decay to which we are led permits us to calculate the shape of the continuous  $\beta$ -spectra by the aid of (6). It contains the quantum number  $j'$  of the absorbed charge as an arbitrary constant which can be determined by comparison of (6) with experiment. In the case of the emission of negative electrons, (6) leads to the general result that  $\mathfrak{F}(W)$  tends to zero near the upper energy limit with an exponential factor of the Gamow type. For a neutrino we should obtain a simple power law. Unfortunately, the measurements available at present are not yet sufficiently accurate to discriminate experimentally between these two possibilities. It may be noticed, however, that a decision will be possible in this way.

From (6) and (7) we can calculate for each quantum number  $j'$  the dependence of the decay constant  $\lambda$  on the upper energy limit  $W_{\max} = \Delta E - mc^2$ . For the heavy radioactive elements we have to assume two quantum numbers giving rise to two curves which can qualitatively be identified with the two curves obtained from Sargent's measurements<sup>(10)</sup>. Extrapolating (6) and (7) to light elements we obtain values of the decay constants which agree fairly well with the order of magnitude actually observed\*. This can be taken as an argument in favour of the general formalism represented by (6) and (7). No decision, however, can be obtained from this about the special character of  $D_2$ .

Care has to be taken in order to account for the excitation of a nucleus by a  $\beta$ -transformation. If the final state of the nucleus after a  $\beta$ -emission is an excited one this means as a rule that the angular momentum balance (2) of the process has been altered. If the excitation energy is small compared with  $\Delta E - 2mc^2$  the probability of transition to an excited state calculated from (6) and (7) will as a rule be considerably larger than the probability of transition to the ground state. This is in agreement with the general experimental evidence. This result is very closely connected with our selection rule discussed in §§ 5 and 8 and can thus be regarded as a strong argument in favour of our assumptions†. Finally it may be noticed that according to (3) no excitation is possible after a  $\beta$ -transformation which involves an excitation energy higher than  $\Delta E - (m + m')c^2$  or  $\Delta E - 2mc^2$  respectively.

Our formulae also allow us to estimate the dimensions of the region within which the production of the electron to be emitted takes place. This estimate, however, does not yield nuclear dimensions as it would in the case of Fermi's theory but suggests a diameter of the order of the Compton wave-length. The result that the  $\beta$ -emission process takes place partially outside the nucleus looks at first rather strange. We must remember, however, that the emission of a wave can never be localized with an accuracy higher than the wave-length divided by  $2\pi$ . This condition is obviously fulfilled.

Our result concerning the localization of the  $\beta$ -emission is a direct consequence of the application of our selection rule for the angular momenta. This shows that our choice of the formally introduced second particle is essential if we want to main-

\* Cf. Dr Sitte's remarks on this point, p. 68.

† Fermi's interpretation of (6) and (7) would account in a similar way for the high excitation probability if we assume that in every  $\beta$ -transition the angular momentum of the nuclear ground state is altered by at least  $2\frac{h}{2\pi}$ .



tain a differential conservation law for the electric charge outside the nucleus. If therefore our application of the selection rule is correct it seems impossible to modify our assumption about the choice of  $D_2$  in (6).

#### § 10. GENERAL CONCLUSIONS

We are thus led to the conclusion that the  $\beta$ -emission can formally be treated as a double process in which a second particle of hypothetical character is assumed to be emitted simultaneously with the  $\beta$ -electron.

General formulae can be derived for these processes which, however, still require arbitrary additional assumptions regarding the nature of the second particle formally introduced, and the angular momenta of the particles involved in the  $\beta$ -transformation.

Two attempts, still of hypothetical character, have been made in this respect:

Fermi desires to maintain the validity of the conservation laws, and thus considers the second particle as a neutrino of mass  $m' = 0$  with an objective existence. This theory is, however, still incomplete and seems to require further additional assumptions in order to account for the experimental data.

Sitte and the author connect the  $\beta$ -transformation with the production of a pair of differently charged electrons. One of these electrons is emitted, the other is captured by the nucleus without conservation of mechanical quantities. An additional selection rule for the angular momenta has to be introduced. This treatment accounts qualitatively for the main features of the  $\beta$ -decay and seems to lead to a fairly complete and consistent picture of the process. Further experimental investigation, however, will be required in order to examine the different arbitrary assumptions.

The  $\beta$ -activity of potassium and rubidium does not fit the regularities found for the other  $\beta$ -bodies and will evidently have to be connected with a more complicated mechanism, possibly with a double process in which two electrons leave the nucleus simultaneously.

#### REFERENCES

- (1) N. BOHR. *J. Chem. Soc. Lond.* 349 (1932) (Faraday Lecture 1930).
- (2) C. D. ELLIS and N. F. MOTT. *Proc. Roy. Soc. A*, **141**, 502 (1933).
- (3) G. BECK. *Nature*, **132**, 967 (1933).
- (4) J. CHADWICK and D. E. LEA. *Proc. Camb. Phil. Soc.* **30**, 59 (1934).
- (5) G. BECK. *Progress of Chemistry*, Moscow 1934. (In the press.)
- (6) G. BECK. *Z. f. Physik*, **83**, 496 (1933); **84**, 811 (1933); K. SITTE. *Phys. Z.* **34**, 627 (1933); G. BECK and K. SITTE. *Z. f. Physik*, **86**, 105 (1933); *Nature*, **133**, 722 (1934).
- (7) E. FERMI. *La Ricerca Scientifica*, **2**, 12 (1933); *Z. f. Physik*, **88**, 161 (1934); G. C. WICK. *Rendiconti Lincei*, **19**, 319 (1934).
- (8) W. HEISENBERG. *Z. f. Physik*, **77**, 1 (1932); **78**, 156 (1932); **80**, 587 (1933).
- (9) J. CURIE and F. JOLIOT. *Nature*, **133**, 721 (1934).
- (10) B. W. SARGENT. *Proc. Roy. Soc. A*, **139**, 659 (1933).
- (11) G. BECK and K. SITTE. *Z. f. Physik*, **89**, 259 (1934); E. FERMI. *Ibid.* **89**, 522 (1934).
- (12) G. BECK. *Z. f. Physik*, **61**, 615 (1930).

# THE $\beta$ -RAY TYPE OF RADIOACTIVE DISINTEGRATION

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**ABSTRACT.** In disintegrations where an  $\alpha$ -particle is emitted, the residual atom may be initially in any one of several energy states, the difference between this energy and that of the ground state being subsequently emitted in the form of a  $\gamma$ -ray. Consequently observation shows groups of  $\alpha$ -particles of definite ranges, with  $\gamma$ -rays of certain frequencies, the differences in energies of the one group corresponding to the differences in the other.

It is pointed out that the same general state of affairs must exist in the case of  $\beta$ -disintegration, except that the emitted particles are no longer homogeneous, but form a continuous spectrum with a sharp upper limit which corresponds to the energy of the  $\alpha$ -particle in the case discussed above.

The argument is to some extent confirmed by recent measurements of Henderson, who has measured the total energy emitted in each of the two branch-reactions by which ThC can change to lead, and has found it equal in the two cases.

The detailed discussion of  $\beta$ -ray disintegration is based on Fermi's theory, in which the neutrino is introduced to maintain conservation of energy, momentum and spin. In this theory, the electron emitted is only created at the instant of disintegration, a neutron in the nucleus at the same time being transformed into a proton. It appears in a semi-empirical way that transitions in which the spin  $i$  does not change are immensely more common than those in which  $\Delta i$  is not zero.

These considerations are applied in detail to the series ThC, ThC', ThC'' and ThD, the energy levels and corresponding spins being assigned.

Similarly in the radium series, a number of states of RaC are set out; for radium C' there are no less than 24 energy states identified up to the present.

Another matter on which a detailed study of  $\beta$ -disintegration can give evidence is the mass of the neutrino. This determines the shape of the high-energy end of the  $\beta$ -ray curves, and conversely, from the measured shape, deductions may be made as to its mass. Henderson's recent results are in favour of a zero value for this quantity, or at most a value many times less than that of an electron.

The final section of the paper is devoted to a detailed discussion of the level systems of certain nuclei, and here it is pointed out that there is some disagreement between the theoretical and experimental values of the internal conversion coefficients.

## § 1. INTRODUCTION

OUR understanding of the details of disintegration processes has been greatly helped by a proper appreciation of the effect of the excitation of the product nucleus. Such effects, most clearly shown in cases of  $\alpha$ -disintegration, appear yet to be of fundamental importance in the  $\beta$ -type, and it is convenient to start by a few general considerations.

We will consider three successive members of a series A, B and C, and will not at this stage specify what disintegration particle is emitted in the disintegration. Suppose A and B and the disintegration particle have mass numbers  $M_1$ ,  $M_2$ , and  $m$  respectively, then  $M_1 = M_2 + m$ . If now the masses of the nuclei and disintegration particle on, for example, the usual oxygen scale, are  $M_1 + \Delta_1$ ,  $M_2 + \Delta_2$ , and  $m + \delta$  respectively and, further,  $W$  and  $w$  are the kinetic energies of the emitted particle and recoil nucleus, then

$$M_1 + \Delta_1 = M_2 + \Delta_2 + m + \delta + \left( \frac{W}{c^2} + \frac{w}{c^2} \right) K,$$

where  $K$  is an appropriate conversion factor depending jointly on the units used for energy and on the mass scale. Hence

$$W + w = \frac{c^2}{K} (\Delta_1 - \Delta_2 - \delta).$$

If the product nucleus is left in an excited state and its mass in that state is

$$M_2 + \Delta_2' \quad (\Delta_2' > \Delta_2),$$

then the total emitted kinetic energy  $W' + w'$  will be less and equal to

$$(c^2/K) (\Delta_1 - \Delta_2' - \delta).$$

In a diagram such as figure 1 the quantities  $\Delta_1 - \Delta_2'$  are represented by the vertical separation of levels  $a_0$  and  $b_0$  or  $a_0$  and  $b_1$ , for example. However, purely for descriptive purposes it is convenient to draw figure 1 so that all of the B states are

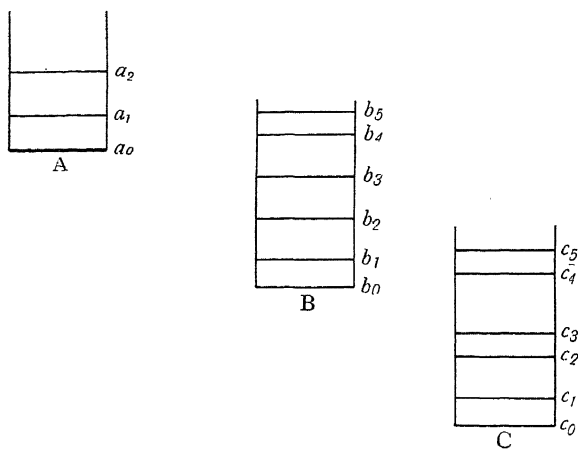


Figure 1.

raised by the  $\delta$  of the appropriate particle emitted in the A-B disintegration. The kinetic energy of the disintegration particle and recoil nucleus for any transition is then represented on the diagram simply by the separation of the appropriate levels  $a_0$  and  $b_0$ , or  $a_0$  and  $b_1$ , for example. Also for shortness from now on reference to the energy of the recoil particle will be omitted.

It is clear that disintegration can occur with excitation of any of the B states up to  $b_3$  but no further. Now suppose B is formed in the  $b_3$  state under emission of a disintegration particle with energy  $a_0 b_2$ , then in the majority of cases the excess energy  $b_2 b_0$  of B will be emitted in the form of  $\gamma$ -rays, and the nucleus B, now in its ground state, will in time change to C in one or other of its excited states. It is however possible for B in its  $b_2$  state to go directly either to the ground state of C or to one of its excited states,  $c_1, c_2 \dots$ . The possible occurrence of these latter transitions was first mentioned by Perrin, but as yet they have not been detected.

When the disintegration particles are  $\alpha$ -particles the above phenomena are shown quite unambiguously. Corresponding to the various possible transitions from  $a_0$  to  $b_3$ , to  $b_2$ , etc., there are found sharply defined groups of  $\alpha$ -particles, and also from B  $\gamma$ -rays of the appropriate energies to correspond. The disintegration  $\text{Th C} \rightarrow \text{C}'$  is the best known case. Since the differences  $b_3 - b_2, b_2 - b_1, b_1 - b_0$  are fairly small compared to  $a_0 - b_0$ , these groups have been named "fine structure" groups. In the same way if  $B \rightarrow C$  is also an  $\alpha$ -disintegration we may have "fine structure"  $\alpha$ -groups corresponding to transitions from  $b_0$  to  $c_0, c_1, c_2, c_3$  or "long range groups" from  $b_3, b_2 \dots$  to  $c_0$  or some other excited state of C. There is no real distinction between these two classes of  $\alpha$ -particle groups, merely one of intensity. The general order of magnitude of the life times of the radioactive elements shows that the majority of the nuclei must reach their ground state, so that transitions from the ground state must be of the order of one per disintegration. Disintegration transitions from excited states have to compete with the possibility of radiative transitions which in general are of the order  $10^4$  to  $10^6$  times more probable. "Long range"  $\alpha$ -particles would therefore only be expected to occur about once in every  $10^4$  to  $10^6$  disintegrations, even under strong excitation of the parent nucleus.

Exactly the same considerations may be applied to the  $\beta$ -disintegration, only here we have the complication that even in the simplest type of disintegration the emitted particles are not homogeneous but form a continuous energy spectrum with however a sharp upper limit of energy  $W$ . This upper limit  $W$  of the continuous spectrum is exactly comparable to the energy of an  $\alpha$ -particle group in the previous discussion, with however one important experimental distinction. The  $\alpha$ -particle groups corresponding to different excitations have sharply defined energies, and can be detected individually with certainty. In the  $\beta$ -ray case we have merely a number of continuous spectra, all starting at about zero energy and ending at different upper limits. The superposition of several such spectra produces a smooth curve of which the only characteristic feature is the upper limit of the highest energy curve.

This statement is not quite correct as it stands and needs amplifying. There are no doubt partial continuous spectra corresponding to the "long range  $\alpha$ -particles," that is, disintegration from excited states. We should again expect these to have a total intensity of the order of one  $\beta$ -particle in  $10^4$  to  $10^6$  disintegrations, and the  $\beta$ -particles of such a weak spectrum spread over an energy range of a few million volts would be extremely difficult to detect. We cannot even assume without investigation that the *observed* upper limit of the composite spectrum necessarily

corresponds to the disintegration transition from ground state to ground state. If this transition is weak, the corresponding  $\beta$ -particles might be too few to give an easily noticeable effect. Cases in point are furnished by  $\text{RaC} \cdot \text{C}'$  and  $\text{ThC}'' \cdot \text{Pb}$ . In the former case transitions to the ground state occur in at most a few per cent of the disintegrations, whereas a level of  $+6.06 \times 10^5$  V. is excited directly in over a third of the disintegrations. The observed upper limit of  $3.2 \times 10^6$  V. corresponds probably to this excitation and the energy separation of the ground states is therefore  $3.2 + 0.6 = 3.8 \times 10^6$  V. In  $\text{ThC}'' \cdot \text{Pb}$  a level of  $+3.2 \times 10^6$  V. is excited in over 90 per cent of the disintegrations, and the observed upper limit of  $1.79 \times 10^6$  V. corresponds to this excitation, giving an available energy of disintegration of  $4.99 \times 10^6$  V.

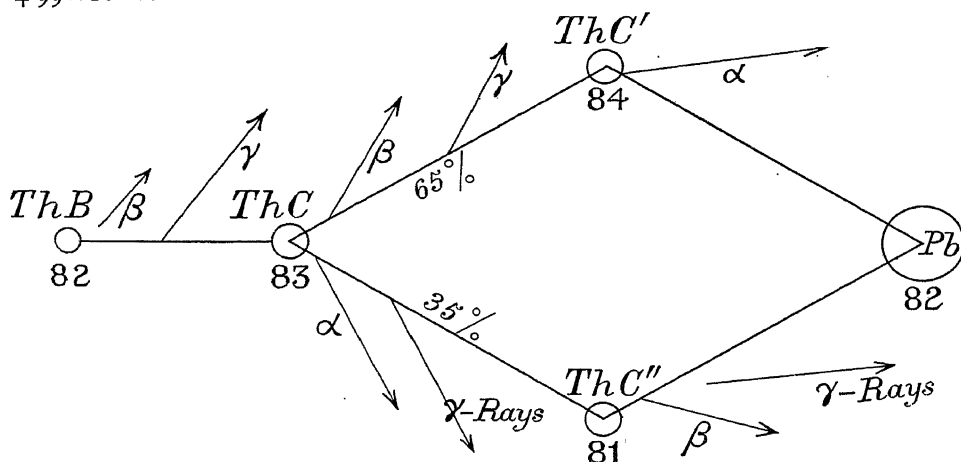


Figure 2.

It will have been noticed that this account of the  $\beta$ -ray disintegration is based entirely on the possibility of applying energy considerations to the upper limits of the spectra. The only evidence on this point comes from some recent measurements of Henderson, working in the Cavendish Laboratory\* which are now in course of publication. By means of a focussing arrangement and special counters he was able to determine unambiguously the separate end-points of the continuous spectra of  $\text{ThC} \cdot \text{C}'$  and  $\text{ThC}'' \cdot \text{Pb}$ . These two bodies occur in the branching scheme shown in figure 2. The excitation of both  $\text{ThC}'$  and  $\text{ThPb}$  is known from the  $\gamma$ -ray spectra and we can be sure that the measured upper limit for  $\text{ThC} \cdot \text{C}'$ ,  $2.25 \times 10^6$  V. corresponds to a transition to the ground state, and the value  $1.79 \times 10^6$  V. for  $\text{ThC}'' \cdot \text{Pb}$  to an excited state of  $3.20 \times 10^6$  V. If, therefore, our assumptions are correct the available energy difference for  $\text{ThC} \rightarrow \text{C}'$  is  $2.25 \times 10^6$  V. and for  $\text{ThC}'' \rightarrow \text{Pb}$   $4.99 \times 10^6$  V., and it also follows that the energy given out along each branch must be the same. The  $\alpha$ -ray energies are well known. For the  $\text{ThC}' \cdot \text{Pb}$

\* Preliminary results were announced at the Solvay Congress of 1933. The final results given here prove the point at issue more precisely.

disintegration we find  $8.95 \times 10^6$  V., giving along the top branch  $11.20 \times 10^6$  V. The  $\alpha$ -ray disintegration Th C.C'' gives out  $6.20 \times 10^6$  V., making a total emission along the lower branch of  $11.19 \times 10^6$  V. The uncertainty in these figures lies mainly in the  $\beta$ -ray data and may be put at  $\pm 0.02 \times 10^6$  V. The agreement is therefore excellent and we can with some confidence adopt this general point of view:

It seems unlikely that results of comparable accuracy will be obtained in the near future for the RaC and AcC branches, since in both cases one branch is of weak intensity, and it is best to follow Henderson's suggestion and to reverse the process. Knowing the total emission along the intense branch and the  $\alpha$ -ray energy emitted in the weak branch, we can by subtraction find the energy emitted by the remaining  $\beta$ -ray body. In this way Henderson finds the energy emitted by RaC''.D to be  $5.89 \times 10^6$  V. This high energy of disintegration is interesting and suggests that there would be frequent excitation of the higher states of RaD, and the possibility must not be left out of account that some of the very weak  $\beta$ -ray lines in the RaC spectrum may be due to  $\gamma$ -rays of RaD.

In the actinium branch Henderson finds that AcC.C' liberates at least  $0.7 \times 10^6$  V. It is only possible to give a lower limit until the excitation of AcPb has been investigated. The present value is deduced on the assumption that the observed upper limit of the AcC''.Pb  $\beta$ -ray spectrum corresponds to a transition to the ground state.

## § 2. THEORIES OF THE $\beta$ -RAY DISINTEGRATION

All attempts at proposing a definite theory of the  $\beta$ -ray disintegration have encountered two serious difficulties, firstly that of describing the behaviour of an electron in the nucleus according to any theory and secondly the necessity of accounting for the continuous spectrum of the emitted  $\beta$ -particles. Recently two theories have been proposed, by Beck\* and Fermi† respectively, and in both of these theories these two difficulties are met by specific assumptions.

In discussing the  $\beta$ -ray disintegrations we shall use Fermi's theory. He supposes that only protons and neutrons exist permanently in the nucleus, the two being considered as different inner quantum states of the one heavy particle, and that it is possible for a neutron to change into a proton with emission of an electron and neutrino. All mechanical quantities are conserved in the process, and the electron and neutrino are assumed to be created at the moment of emission, the emission being somewhat analogous to that of a light quantum by an excited atom. According to this theory the disintegration constant  $\lambda$  is

$$\lambda = A \left| \int u_n v_m^* d\omega \right|^2 F(\eta),$$

where  $u_n$  and  $v_m$  are the eigenfunctions of the nuclear neutron and resultant proton and  $F(\eta)$  is a function of  $\eta = H\rho/1700$  where  $H\rho$  refers to the upper limit of the spectrum. The factor  $\left| \int u_n v_m^* d\omega \right|^2 \dots$  will be of the order of unity if the initial and resultant nuclei possess the same spin, and would be expected to be reduced by a

\* Beck, *Z. f. Physik*, **83**, 496 (1933); **84**, 811 (1933); Beck and Sitte, *ibid.* **86**, 105 (1933).

† Fermi, *Z. f. Physik*, **88**, 161 (1934).



cussed in §4, whilst spin differences from one body to another have been adjusted in the manner suggested by Gamow. He points out that owing to the absence of fine structure in the  $\alpha$ -disintegration series leading to Th B, it follows that the spin has not changed and we therefore take it to be zero. We now consider the  $\beta$ -disintegration of Th B. C. The detectable upper limit  $3.62 \times 10^5$  V. of the  $\beta$ -ray spectrum clearly corresponds to the strong excitation (0.95) of the state with energy,  $+2.38 \times 10^5$  V., so we deduce an energy of disintegration of  $6.0 \times 10^5$  V. The upper limits  $E_\beta$  of the other  $\beta$ -ray spectra corresponding to excitation of the other states are at once obtained and are shown in the next table. In the neighbouring column are given values of Fermi's function  $F(\eta)$ . The partial disintegration constants for the different excitations are simply the excitations  $p$  multiplied by the disintegration constant  $\lambda$  of Th B. In the last column is placed the ratio of  $p\lambda \times 10^8$  to  $F(\eta)$  and this quantity should be proportional to  $|\int u_n v_m^* d\omega|^2$  and be high when the spin does not change.

## Th B. C

$$E_{\text{dis}} = 6.0 \times 10^5 \text{ V.}; \lambda = 1.82 \times 10^{-5} \text{ sec.}^{-1}$$

Energy of state of Th C (V. $\times 10^{-5}$ )	Spin	Excitation $p$	$E_\beta$	$F(\eta)$	$p\lambda \times 10^8$	$\frac{p\lambda \times 10^8}{F(\eta)}$
4.14	0	0.05	1.86	0.021	91	4,300
2.99	2	0	3.01	—	0	—
2.38	0	0.95	3.62	0.166	1730	10,400
0	2	0	6.0	—	0	—

Now in considering such calculations it must be remembered that the values for small excitations obtained from  $\beta$ -ray data are at present very inexact. The value for the top level is a lower limit and it might be as high as 0.1. The values, zero, for the second and ground levels mean only extremely small excitation. The results therefore support the view shown in figure 3 that the main disintegrations from the ground state of Th B ( $i=0$ ) go to the states 4.14 and 2.38 with also  $i=0$ . The absence of disintegrations to the other two states is explained by their spins ( $i=2$ ) which values are required *on other evidence* to account for the intensities of the  $\gamma$ -rays. It is also interesting to note how the very different excitations of the two  $i=0$  states is largely explained by the difference in the amount of energy released.

From considerations of fine structure in the  $\alpha$ -rays from Th C, Gamow has shown that we must assign spins to Th C'' as shown. These values are consistent with the  $\gamma$ -ray intensities. Further, in the disintegration Th C''. Pb, the top level of Th Pb appears to be excited at every disintegration. For this disintegration the quantity  $p\lambda \times 10^8 / F(\eta)$  comes to be 8700, and the agreement with the Th B values shows that in this disintegration  $\Delta i=0$ . The spin of the top level of Th Pb is therefore 4, and the remaining spins are inserted from  $\gamma$ -ray data. It will be noticed that we should not expect any noticeable transitions to level 5.82 ( $\Delta i=2$ ). From the  $\beta$ -ray data we find that there is a possibility of some slight direct excitation of levels 5.10 and 2.76 which, if confirmed, would be compatible with a  $\Delta i=1$ . The ground state of Th Pb



is given a spin 1, following Gamow, in spite of the spectroscopic evidence that there is no hyperfine structure. He suggests that it is reasonable to assume that the corresponding Landé factor vanishes\*.

The absence of fine structure in the  $\alpha$ -rays from ThC' shows the ground state of ThC' to have the same spin as that of ThPb. The values for the other states and the excitations are obtained from  $\gamma$ -ray data. The values for  $p\lambda \times 10^8/F(\eta)$  for the four states starting at the top are respectively 625, 415, 80 and 95. These low values (compared to about 9000 for ThB.C and ThC''.Pb) are compatible with  $\Delta i \neq 0$  required by the diagram.

In considering this evidence it must be remembered that the values for weak excitations are uncertain, that the form of  $F(\eta)$  is only a first approximation based on specific assumptions, and that the quantity

$$\frac{p\lambda \times 10^8}{F(\eta)} = \left| \int u_n v_m^* d\omega \right|$$

is bound to fluctuate largely according to the detailed characteristics of the states so that considerations of the change of spin can only set limits to its general order of magnitude. We must conclude therefore that closer examination entirely confirms Fermi's arguments in favour of his theory and also the use Gamow has made of them to follow the changes in spin from element to element. We may reasonably hope, when further developments have given a more secure basis to the function  $F(\eta)$ , and when, on the experimental side, the excitations have been determined more accurately, that this method may be employed to measure the matrix element of the switch.

Some interesting points emerge when similar considerations are applied to the radium series. The values applicable to RaB.C are shown in the next table.

#### RaB.C

$$E_{\text{dis}} = 10.0 \times 10^5 \text{ V.}; \lambda = 4.31 \times 10^{-4} \text{ sec.}^{-1}$$

Energy of excited states of Ra C (V. $\times 10^{-5}$ )	Spin	Excitation $p$	$\frac{p\lambda \times 10^8}{F(\eta)}$
3.499	0	0.52	17,800
2.937	0	0.47	12,400
2.571	2	0.01	230
0.529	2	0	0
0	2	0	0

The relative spin values, as before, are settled on  $\gamma$ -ray evidence, and we give the value  $i=0$  to the two top states, since they are clearly formed by permitted transitions and, as in the case of ThB, we may assume the spin of the ground state of RaB to be zero. It is possible that the excitations are too high by about 10 per cent and

\* This conclusion has been criticized by Elsasser on the grounds that all stable nuclei with even numbers of both protons and neutrons have zero spin. It is difficult to see how to apply consistently both this rule and the present views on the effect of spin changes on the  $\alpha$ - and  $\beta$ -disintegration probabilities. This matter is being further investigated.

that there is some slight excitation of the lower states. These would clearly fit in with forbidden transitions.

From quite independent evidence we know that the spin of the ground state of  $\text{RaC}'$  formed in the  $\text{RaC.C}'$  disintegration is zero, so that in this case the absolute spin values are fixed. The level system of  $\text{RaC}'$  is very complicated\*, having twenty-four states, and as the excitations are mostly only a few per cent, we could scarcely expect to find much regularity at the present stage of the theory. There are only two states with reasonable excitation. One with 15 per cent excitation, energy  $28.81 \times 10^5$  V. and spin 2, gives the highest value for  $p\lambda \times 10^8/F(\eta)$ , viz. 2800, which, although much below the  $\text{RaB.C}$  values, is not incompatible with a permitted transition from the  $\text{RaC}$  ground state, also with spin 2. The other state with about 40 per cent excitation, energy  $6.06 \times 10^5$  V., and spin 1, gives a value 60, clearly indicating a forbidden transition; in this case  $\Delta i = 1$ .

Finally it may be mentioned for comparison that the disintegration  $\text{RaE.F}$ , when there is no excitation, gives a value for  $p\lambda \times 10^8/F(\eta)$  of 14, indicating a forbidden transition.

It is also interesting to discuss certain points about the form of the  $\beta$ -ray spectra in the light of Fermi's theory, although we have not yet sufficiently accurate measurements to enable any definite conclusions to be drawn. It will at once be appreciated that the measured distribution is in general a superposition of several partial spectra. The simplest preliminary assumption is that except for a varying extension along the energy scale, all partial  $\beta$ -ray spectra are of the same shape, but to this Fermi's theory adds the important remark that the shape will be different for permitted ( $\Delta i = 0$ ) and forbidden transitions ( $\Delta i \neq 0$ ). This seems to fit in with some results found by Ellis and Mott†. The  $\text{RaC.C}'$   $\beta$ -ray spectrum differs noticeably from that of  $\text{RaE.F}$  (no excitation), but these differences are largely removed if we consider the  $\text{RaC.C}'$  curve to be built up of partial  $\text{RaE.F}$ -like curves with intensities corresponding to the excitations. This is reasonable, since many of the  $\text{RaC.C}'$  components are forbidden transitions like the simple  $\text{RaE.F}$  curve. An attempt to build up the experimental  $\text{ThC.C}' + \text{ThC''}. \text{Pb}$  spectrum from  $\text{RaE.F}$ -like curves failed and we can see one reason in that the  $\text{ThC''}. \text{Pb}$  will be a simple permitted spectrum and therefore unlike a  $\text{RaE.F}$  curve. It is interesting to note that the divergence lay in the calculated curve falling too quickly at low energies; the theory suggests precisely this difference, that is, that curves corresponding to forbidden transitions like  $\text{RaE.F}$  will fall off more sharply than those for permitted transitions like  $\text{ThC''}. \text{Pb}$ .

It is important to obtain some reliable information about the lower energy portions of these curves, particularly since the calculated state is independent of what we assume about the mass of the neutrino. Unfortunately such measurements are very difficult.

Wick‡ has applied Fermi's theory to the positron disintegration of the artificial

\* See figure 7.

† Ellis and Mott, *Proc. Roy. Soc. A*, **141**, 502 (1933).

‡ Wick, *Rend. Accad. Lincei*, vi, **19**, 319 (1934).

radioactive elements and here there seems to be some disagreement. Ellis and Henderson\* found that in the positron spectrum from radiophosphorus there appear to be few, if any, positrons with energy less than 200,000 V., whereas theory suggests a smooth fall to zero energies with an exponential drop only below 10,000 V. In discussion Dr Peierls has informed me that it would probably be necessary to take a different form for the Fermi force to account for this result.

The  $\beta$ -radioactivity of potassium and rubidium raises many interesting points, of which the most prominent is the contradiction between the long lifetime of these bodies and the high energy of emission of the particles. Various attempts to explain this have been made from time to time, such as Gamow's suggestion that the disintegration involved the simultaneous emission of two  $\beta$ -particles. This idea has been carefully investigated by Klemperer, working in the Cavendish Laboratory, but he was not able to find any indication of dual emission. He has also investigated various other suggestions, but as yet his experiments have not provided a solution of the difficulty.

### § 3. THE NEUTRINO HYPOTHESIS

The existence of the continuous spectrum of  $\beta$ -rays in the  $\beta$ -ray type of disintegration implies either that the conservation of energy does not apply, or that energy in some hitherto undetected form is emitted. Many years ago Pauli suggested that this energy might be carried by a certain particle, which he called the neutrino, whose properties were such as to make it extremely difficult to detect. It was to have a mass small compared to the electron, no charge but the same spin as the electron. All attempts to detect such particles have failed. Chadwick and Lea†, by investigating the residual ionization from RaE surrounded by several centimetres of lead, concluded that a neutrino could not form as much as one pair of ions in 150 km. of air at N.T.P. Even if subsequent similar experiments do detect a small residual ionization, it seems clear that the neutrino can scarcely be prominent as an experimental particle until some more easily measurable interaction with matter is discovered. For example, it is conceivable that neutrinos might be captured by nuclei and thereby provoke disintegrations, but Peierls and Bethe‡ have pointed out that theoretically this seems very improbable and no such results have been reported.

However, Fermi has shown how helpful the neutrino hypothesis can be in a theoretical treatment of the  $\beta$ -ray disintegration. The emission of a neutrino is supposed to accompany the emission of each  $\beta$ -particle with the appropriate energy necessary for conservation of energy in the whole process. The neutrino here can either be regarded as an actual particle or alternatively as summing up in a convenient form the divergence between theory and fact. Supposing the neutrino not to exist, and that therefore there is no conservation of energy, it would still be a result of the highest importance to know just how accurately the introduction of the neutrino enabled theory to describe different details of the disintegration.

\* Ellis and Henderson, *Proc. Roy. Soc. A*, **146**, 206 (1934).

† Chadwick and Lea, *Proc. Camb. Phil. Soc.* **30**, 59 (1934).

‡ Peierls and Bethe, *Nature*, **133**, 532 (1934).

The one disposable parameter is the mass  $\mu$  of the neutrino and we can form estimates of its magnitude from the shapes of the continuous  $\beta$ -ray curves. Perrin has pointed out that general considerations of the conservation of energy and momentum suggest that the curve would be the more asymmetrical with its maximum shifted to lower energies the smaller the mass of the neutrino in relation to the mass of the electron. Now the position of the maximum at low energies is just what is found in all  $\beta$ -ray spectra, and also in positron spectra from artificial radioactive elements. An actual estimation of the neutrino mass from the shapes of the curves will require careful consideration of the various factors mentioned in §2, such as the possible composite nature of the spectrum, the occurrence of permitted or forbidden transitions, and the particular form assumed for the Fermi field.

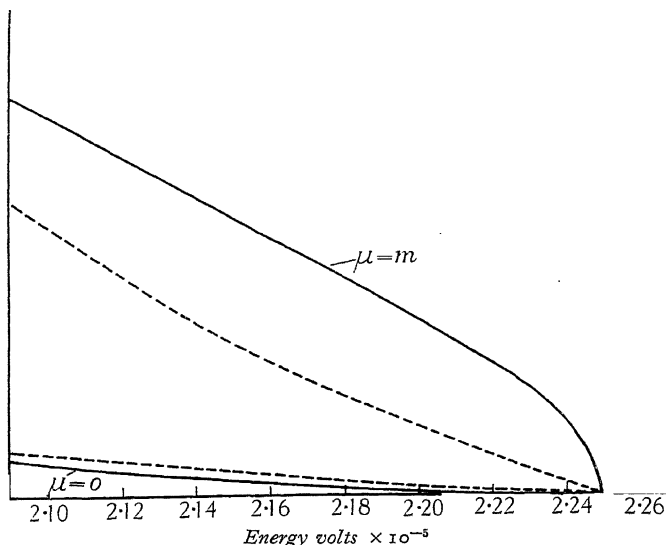


Figure 4. ThC.C'. Full curves theoretical. Dotted curves experimental.

Fermi has pointed out that the shape of the curve in the immediate neighbourhood of the upper limit is very sensitive to the mass of the neutrino and to a first approximation is independent of the character of the transition. Further, from an experimental standpoint it should be noted that just this part of a composite curve will be free from overlapping and represent the upper portion of the highest energy partial curve. The most accurate determination of the shape of the ends of continuous spectra are those of Henderson for ThC.C' and ThC''.Pb, using the semicircular focussing method and counters, and he has recently compared\* his measurements with the formulae given by Fermi. Great care is necessary in handling the experimental results to take into account properly the effects of the size of the defining slit and the slit over the counter. It is by no means sufficient to take the

\* Unpublished. I am very grateful for permission to include his results in this report.

counts obtained in different magnetic fields and to divide these by  $H$  in order to compensate for the varying collecting power of the counter. It is also necessary to make detailed investigation of the form of the curve which would be obtained from a homogeneous source of electrons.

Henderson's method was one of successive approximations, gradually altering the distribution curve until he had obtained one which, taking into account the actual dimensions of his apparatus, would reproduce closely the actual curve of counts against magnetic field. His results for  $\text{Th C.C'}$  and  $\text{Th C''}. \text{Pb}$  are shown in

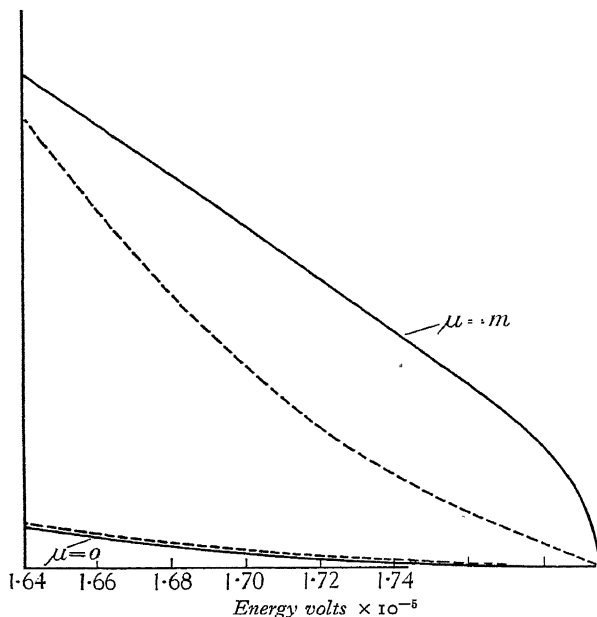


Figure 5.  $\text{ThC''}. \text{Pb}$ . Full curves theoretical. Dotted curves experimental.

figures 4 and 5, where the full lines represent Fermi's formulae for zero and electronic mass of the neutrino respectively and the dotted lines indicate the run of the reduced experimental curve, drawn twice so as to fit in turn each theoretical curve at the end-point and at a point 0.9 of the maximum energy. The results as presented are in favour of a zero rest mass for the neutrino, and after considering the inevitable uncertainties in counting measurements at the extreme end of a curve, this conclusion can still be maintained. Henderson has also analysed Gurney's\* measurements for  $\text{RaC.C'}$  made in 1925, but his results in this case while favouring a zero mass are not conclusive. Gurney\* used a Faraday cylinder and electrometer to detect the electrons and was forced to have very wide slits and small radius of curvature, and this renders the deduction of the true distribution curve far more doubtful.

\* Gurney, *Proc. Roy. Soc. A*, 109, 540 (1925).

## § 4. THE LEVEL SYSTEMS OF CERTAIN RADIOACTIVE NUCLEI

In § 2 we have shown the level systems of ThC, ThC', ThC'', ThPb and RaB. The arrangement of the states and their energies have been discussed on several occasions\*, the more interesting features which we are now beginning to determine with some certainty being the relative spins and initial excitations of the states. These depend largely on the absolute values of the internal conversion coefficient, and the absolute intensities of certain strong  $\beta$ -ray lines. Only a few direct measurements of

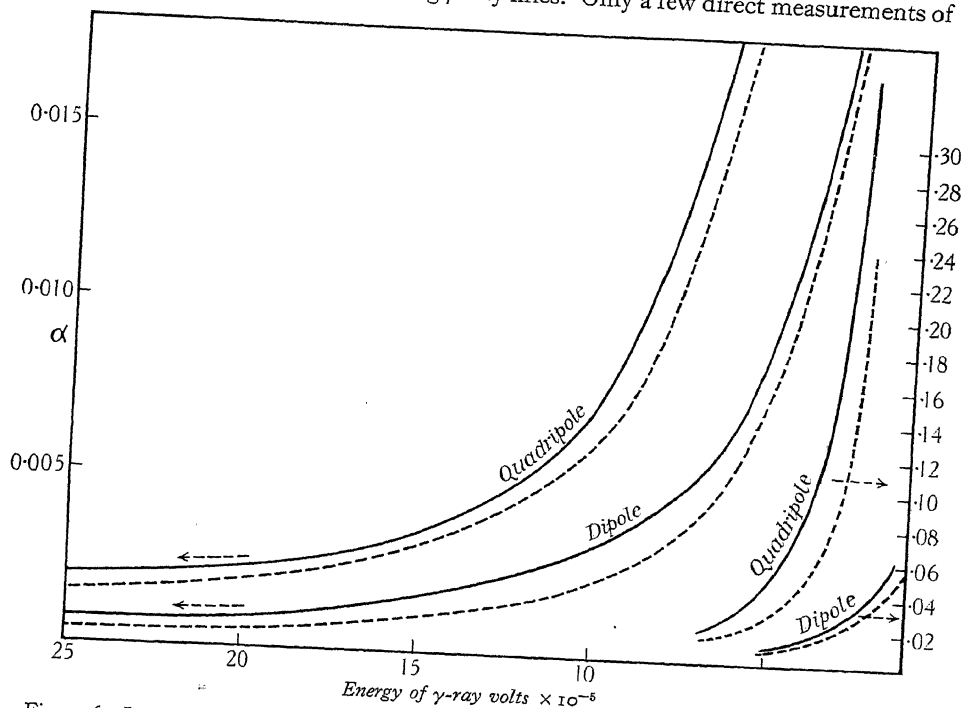


Figure 6. Internal conversion coefficient. Full curves experimental. Dotted curves theoretical.

the internal conversion coefficient have been made and we are forced to a rather laborious system of successive adjustments and approximations in order to set up both a curve showing the variation of this coefficient with frequency and excitation schemes for the various nuclei which are consistent with a variety of data about the  $\gamma$ -ray emission.

It is well known from the work of Mott† and his collaborators that we must take into account both dipole and quadrupole transitions and that there is an appropriate internal conversion curve for each type. Experiment also shows two sets of internal

\* Gamow, *Nature*, **126**, 396 (1930); Ellis, *Proc. Roy. Soc. A*, **136**, 396 (1932); **138**, 318 (1932); Ellis and Mott, *Proc. Roy. Soc. A*, **139**, 369 (1933).

† For references see *Proc. Roy. Soc. A*, **146**, 178 (1934).

conversion values, which we identify with these two types of transitions, but the experimental curves lie definitely above the theoretical ones\*. Oppenheimer, of the Cavendish Laboratory, has recently examined all the experimental evidence, and his experimental curves for the variation of the internal conversion coefficient are shown in figure 6. The arguments and data used are too detailed for inclusion in this report, but will be published shortly. Figure 6 also includes the theoretical curves and it is an urgent and interesting problem to find how the theory can be brought more into agreement with experiment.

The use of this curve in setting up a level scheme with its excitations and spin, and the method of using the various data, can best be illustrated by considering the case of RaC'. This problem has also been treated by Oppenheimer, and his provisional results are shown both in the next table and in figure 7.

We start by knowing twelve levels from the existence of long range  $\alpha$ -particle groups emitted by RaC'. These however are not sufficient to accommodate the fifty-eight  $\gamma$ -rays of RaC' and it is necessary to put in more levels. The main help at this stage is to find combinations between the  $\gamma$ -rays of the type  $h\nu_1 + h\nu_2 = h\nu_3$  or  $h\nu_4 + h\nu_5$ . A rather large tolerance must be allowed in the energy fit since the  $\gamma$ -ray energies are only known to about one part in 500, and as a result a variety of different level systems can be proposed. Oppenheimer for example found nine possible systems. We must not assume that the system with the smallest number of extra levels is necessarily the best, but must instead use the evidence from intensity measurements. For nine of the strong  $\gamma$ -rays the intensities have been measured directly; for the remainder we must take the intensities of the  $\beta$ -ray lines and divide by the internal conversion coefficient. But now for any frequency there are always two values of the coefficient according to whether the transition involves a change of one or two units of spin, so simultaneously it is necessary to assign spin values to the different levels. Once this is done (in such a way that impossible transitions  $\Delta i > 2$  do not occur) we can then find the excitation of each level from the excess of the intensities of the  $\gamma$ -rays leaving it over those of the  $\gamma$ -rays ending on it. Clearly negative intensities must not occur, and further the total excitation must be close to unity†. Lastly the total energy emitted must agree with the measured value.

It will easily be seen that, using these criteria, there is not much ambiguity in deciding whether a level system is correct or not. Eight of the systems tried for RaC' were ruled out quite definitely, the remaining one shown in figure 7 seems promising, but will require a number of check measurements on special points in order to substantiate it. We will consider briefly the extent of the agreements. Twelve levels are added to the twelve  $\alpha$ -ray levels and with these all but three of the fifty-eight  $\gamma$ -rays are fitted in, and these three  $\gamma$ -rays are all extremely weak. Twenty-two  $\gamma$ -rays are fitted to better than  $0.01 \times 10^5$  V., fourteen to better than  $0.02 \times 10^5$  V., seven to better than  $0.03 \times 10^5$  V., seven to better than  $0.04 \times 10^5$  V., and five to

\* There is some evidence that the experimental curves should be raised still more by a few per cent.

† A little latitude is permissible to allow for the general scale of the  $\beta$ -ray intensities being in error.

## Nuclear Levels of RaC'

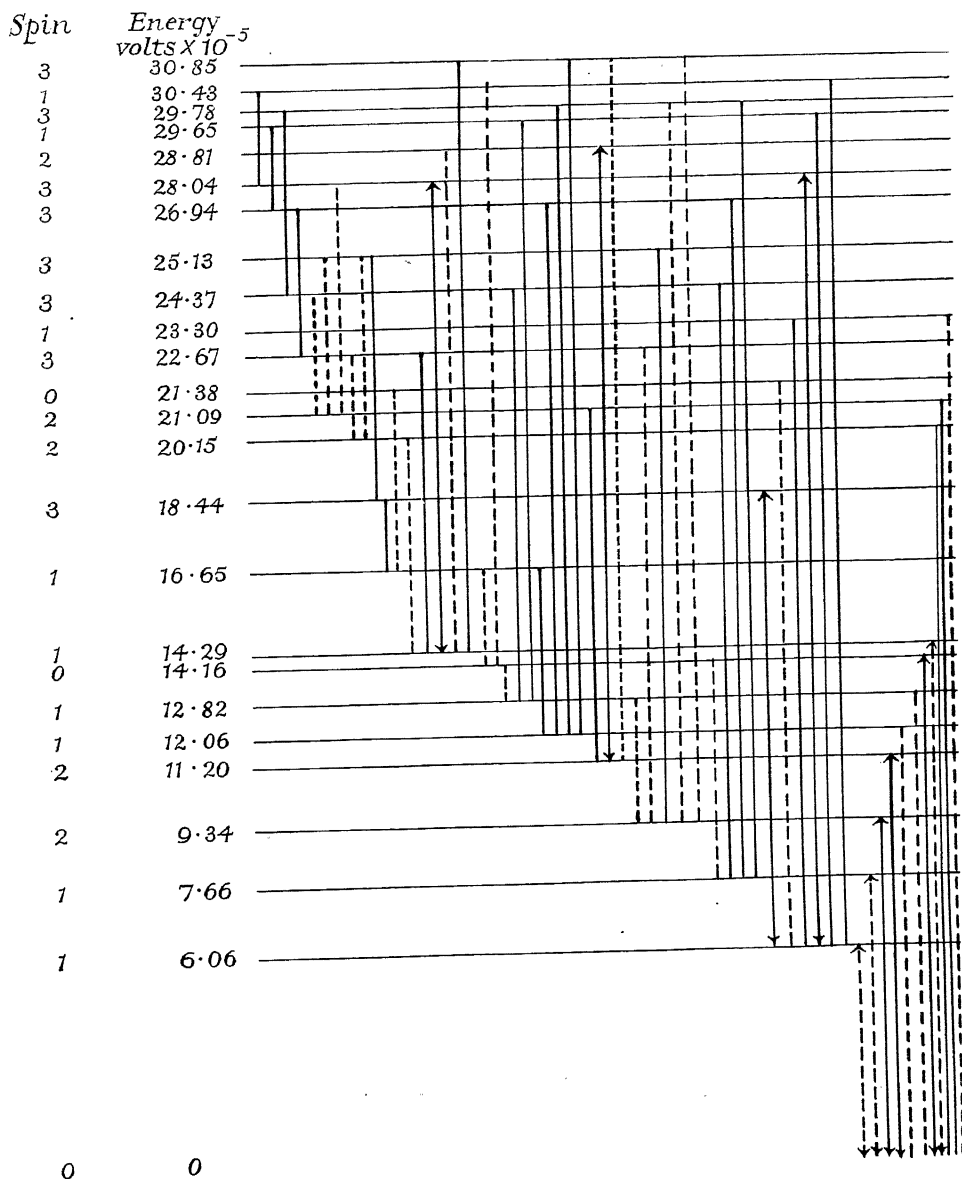


Figure 7. Full lines show quadrupole transitions. Dotted lines show dipole transitions.  
Strong  $\gamma$ -rays shown by arrows.



better than  $0.045 \times 10^5$  V. Of the nineteen  $\gamma$ -rays showing differences in energy greater than  $0.02 \times 10^5$  V. only one is of such intensity that the disagreement is serious at this stage of the work; the other eighteen  $\gamma$ -rays are all weak and difficult to measure.

*Level system of RaC'*

Energy of state $V. \times 10^{-5}$	Spin	Excitations		
		I	II	III
30.85	3	0.058	0.049	0.035
30.43	1	0.028	0.024	0.018
29.78	3	0.066	0.056	0.043
29.65	1	0.018	0.015	0.012
28.81	2	0.156	0.132	0.140
28.04	3	0.088	0.075	0.056
26.97	3	0.010	0.009	0.007
25.13	3	0.029	0.025	0.021
24.37	3	0.021	0.018	0.016
23.30	1	0.043	0.036	0.032
22.67	3	0.014	0.012	0.010
21.38	0	0.016	0.014	0.012
21.09	2	0.016	0.014	0.014
20.15	2	0.018	0.015	0.017
18.44	3	0.050	0.043	0.046
16.65	1	0.019	0.016	0.017
14.29	1	-0.001	0	0.004
14.16	0	0	0	0
12.82	1	0.014	0.012	0.016
12.06	1	-0.002	0	0.009
11.20	2	0.005	0.004	0.009
9.34	2	-0.003	0	0.009
7.66	1	-0.006	0	0.009
6.06	1	0.413	0.350	0.454
0	0	0	0.081	0

Next we consider the excitations. The first values obtained directly from the measured intensities of the  $\beta$ -ray lines and the internal conversion coefficients, dipole or quadrupole according to the spin values, are shown under I. It will be noticed that there are only four negative excitations and these are all small. In each of these cases several weak  $\gamma$ -rays are involved and subject to future investigation we may attribute this discrepancy to errors in estimating the intensities of weak  $\beta$ -ray lines. The total excitation is 1.07 including the negative values, or 1.082 writing them as zero. The total energy emitted however comes to be 15 per cent too high. The excitations under II are obtained by reducing those under I by this 15 per cent, giving a total excitation of 0.92 and hence leaving 0.08 for direct transition to the ground state. We think some reduction in this sense will be necessary since the measurement of the total energy emitted is unlikely to be 15 per cent in error; at the most 2 or 3 per cent could be allowed. To account for this reduction, we should then have to assume that all the  $\beta$ -ray intensities are 15 per cent too high. This is a point that has been suspected for some time; in fact all our  $\beta$ -ray intensities are based on just one determination of Gurney's\* made nine years ago. In view of the

\* Gurney, *Proc. Roy. Soc. A*, 109, 540 (1925).

importance that now attaches to this measurement it is certainly time that it was repeated.

There is another possible source of error in the excitations I which might account for the discrepancy in the energy emission. The absolute values for the  $\beta$ -ray intensities corresponding to the high energy  $\gamma$ -rays are obtained only by step-wise comparison in several stages with Gurney's fundamental value. If as a result there had been a systematic error of a few per cent in each comparison leading to too large intensities for the high speed  $\beta$ -rays, then the total energy emitted would be at once reduced.

In order to indicate the type of alterations that occur we have included in the table, under III, a set of excitations where the error in the total energy resulting from scheme I is corrected partly by the method just indicated and partly by reducing all the  $\beta$ -ray intensities by 7 per cent.

An interesting feature of this level system is that it seems possible to separate it into two practically non-combining systems, but it is of little use to discuss this before the system has passed the test of further experimental work.

It is also possible to connect together the intensities of the long-range  $\alpha$ -ray groups and the  $\gamma$ -ray intensities, but the calculations on this point are not sufficiently advanced for inclusion in this report.

Whether this particular level system can be maintained or not, it shows the possibility of advance along this line. One of the merits of the work is that it provides a guide and interest for further work in  $\beta$ -ray spectroscopy by directing attention to special points; without some guide, progress would be almost impossible in view of the complexity and extreme detail of the experimental material. It must be remembered that it is likely to be a long time before we can obtain anything like such detailed data for other non-radioactive nuclei.

The level systems with the appropriate spin and excitation data of the other nuclei shown in figure 3 have been obtained by an application of the same principles and need not be discussed in detail. There appears to be nowhere any marked discrepancy between the results of deducing spin and excitation data from the  $\gamma$ -ray and from the  $\alpha$ - and  $\beta$ -disintegration measurements, but there are many small points that need clearing up and many quantities that need remeasurement before we can be sure whether the general point of view which has been put forward leaves any major factor out of account.

# GENERAL STABILITY-PROBLEMS OF ATOMIC NUCLEI

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**ABSTRACT.** The conditions for stability of a nucleus, considered as built up from neutrons and protons, are that energy shall not be gained in the emission of either a neutron or a proton. The first condition is satisfied for all atomic numbers, and the second for atomic numbers up to about 200. Consequently known nuclei must be stable with respect to emission of these particles.

As regards the emission of an  $\alpha$ -particle, constructed of two neutrons and two protons, the condition is that the energy necessary to extract these four particles from the nucleus must exceed the energy obtained in the formation of the particle (i.e. its mass-defect relative to the neutrons and protons composing it, in energy units).

It is shown by a definite example that reactions which are possible from energy considerations may be so infrequent as to be practically unable to occur.

In the case of beryllium of mass 9, which "ought" to break up into two  $\alpha$ -particles and a neutron, an explanation is possible if we assume that the nucleus contains an unobserved particle, the negative proton, together with five protons and three neutrons. In this case the disintegration cannot occur, because there are not sufficient neutrons present to form the two  $\alpha$ -particles. Other arguments for the existence of the negative proton are provided by the existence of isotopic isobars such as RaD and the stable lead atom of mass 210.

When the possibility of the emission of positive as well as negative electrons is considered, the stability condition becomes restricted to a relatively narrow band on a diagram in which  $n_1/n_2$  is plotted against  $(n_1 + n_2)$ , where  $n_1$  and  $n_2$  are the numbers of neutrons and protons respectively.

Such a diagram, showing all known isotopes, is plotted, and it is found that in general the radioactive elements lie in the parts of the diagram where they would be expected on theoretical grounds.

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ACCORDING to the modern views on nuclear constitution, the nuclei of different elements are built up from a certain number of elementary heavy particles: neutrons, ordinary protons and probably, to some extent, by unobserved negative protons.

The motion of these heavy particles can be described by the ordinary laws of wave mechanics and, making certain plausible hypotheses about the forces between them, Heisenberg succeeded in explaining some general features of nuclear constitution and obtained an approximate expression for the binding energy of the nucleus as a function of the number of neutrons ( $n_1$ ) and protons ( $n_2$ ) in it.

This expression is in general agreement with the mass-defect curve as obtained from Aston's measurements and shows that the absolute value of the total nuclear binding energy (the energy itself being always negative) increases with the atomic weight. Turning our attention to the absolute value of the binding energy of a neutron or proton separate from the nucleus, we find that the former is nearly

constant throughout the whole range of known elements, while the latter decreases with increasing atomic number. This can easily be understood if we remember that the repulsive Coulomb forces between the proton and the nucleus (not existing in the case of the neutron) increase with the nuclear charge and relax the binding of a proton to the nucleus. However, these repulsive forces can overbalance the nuclear attraction only for a very high nuclear charge ( $Z$  about 200) and we have no reason to expect the spontaneous emission of protons by known nuclei. Writing  $E(n_1, n_2)$  for the total binding energy of the nucleus, we can formulate the condition for stability concerning the emission of nuclear neutrons and protons in the form:

$$-\frac{\Delta E}{\Delta n_1} > 0 \quad \dots\dots(1)$$

and

$$-\frac{\Delta E}{\Delta n_2} > 0 \quad \dots\dots(1').$$

The first condition will be satisfied for any atomic number and the second will fail only for  $Z \sim 200$ . The stability condition concerning the emission of a complex particle (such as an  $\alpha$ -particle) may be formulated by saying that the energy necessary to extract from the nucleus in question a certain number of neutrons and protons must be larger than the energy set free in the formation of the emitted particle.

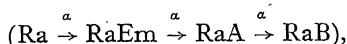
Thus the condition for  $\alpha$ -stability will be

$$-2 \left( \frac{\Delta E}{\Delta n_1} + \frac{\Delta E}{\Delta n_2} \right) > \Delta M_{\alpha} \cdot c^2 \quad \dots\dots(2),$$

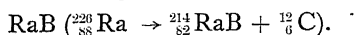
where  $\Delta M_{\alpha}$  is the mass-defect of the  $\alpha$ -particle as constructed from two neutrons and two protons. We see that the condition (2) can be violated for much smaller atomic numbers than the conditions (1) and (1'), and as a matter of fact  $\alpha$ -disintegration takes place as early as  $Z \geq 83$ .

If there were no irregularities in the nuclear structure, we should expect that no spontaneous  $\alpha$ -disintegration would be possible for  $Z$  smaller than a certain limit, and that the energy set free in  $\alpha$ -disintegration would increase regularly with increasing atomic number. In reality this is not so: a case of  $\alpha$ -disintegration is known for comparatively small atomic number ( $\alpha$ -activity of samarium,  $Z = 62$ ) and in the region of radioactive elements the maximum energy of disintegration is observed for the nuclei ThC', RaC' and AcC' located next to the limit of  $\alpha$ -stability. We shall return later to these irregularities connected with periodicity in the nuclear structure.

It is interesting to notice that for the nuclei of known radioactive elements, not only  $\alpha$ -emission but also the emission of heavier particles is possible on energy considerations. For example Ra, instead of emitting three successive  $\alpha$ -particles



can emit the nucleus of carbon, being transformed directly into



The energy of this reaction must be equal to the sum of the disintegration energies for three successive  $\alpha$ -emissions plus the binding energy of three  $\alpha$ -particles in the carbon nucleus. Thus we get for this energy

$$4.85 + 5.53 + 6.07 + 2.70 = 19.15 \times 10^6 \text{ e.V.}$$

Calculating, according to the wave-mechanical formula, the decay constant for such disintegration we obtain the value:  $\lambda_c \sim 10^{-45} \text{ sec}^{-1}$ . Remembering that the decay constant of radium for  $\alpha$ -emission is  $\lambda_\alpha = 1.37 \times 10^{-11} \text{ sec}^{-1}$  we come to the conclusion that the number of carbon nuclei emitted by Ra must be  $10^{+34}$  times smaller than the number of  $\alpha$ -particles, which makes it practically impossible to observe.

Thus we see that, especially in the region of the heavy elements, reactions can occur which, although possible from energy considerations, possess such small probabilities that they have no chance of being observed.

This, however, does not hold for light nuclei where the potential barriers are not high enough to prevent the escape of nuclear particles with energy of several million volts. The characteristic example of such a case is the stability puzzle of the beryllium nucleus.

Accepting for the mass of this nucleus Bainbridge's value 9.015 and for the mass of the neutron Chadwick's value 1.0068, which seems to be generally accepted at present, we find that the spontaneous disintegration of the beryllium nucleus into two  $\alpha$ -particles and one neutron,



should occur with the liberation of about  $5 \times 10^6 \text{ e.V.}$  of energy.

We cannot find in this case any potential barrier of reasonable height to prevent the splitting of the nucleus, and it should disintegrate in an extremely small fraction of a second. We know, however, that this does not happen, and if, as shown by Lord Rayleigh, there are some indications of an instability of beryllium, nobody doubts that this element has a fairly long life period. A plausible explanation of this difficulty can be based on the hypothesis, put forward by the author, according to which the new kind of particles, the negative protons (symmetrical to the ordinary protons in respect to neutrons) can be present in nuclear structure. As was indicated by Pauli at the discussion in Copenhagen (and later mentioned independently by Dirac) the Be-nucleus will be stable if we suppose that it contains one negative proton



In this case the reaction  $B \rightarrow 2\alpha + n$  is not possible as there are not enough neutrons to form two  $\alpha$ -particles.

We may anticipate that the internal transformation  $p^+ + p^- \rightarrow 2n$  could occur in the nucleus, the result of which would be the immediate splitting of the resulting isomeric nucleus into two  $\alpha$ -particles and a neutron. However, the probability of such simultaneous transformations of two heavy particles must be expected to be very small and the Be-nucleus may exist for a fairly long time. From this point of view the life period of beryllium depends on the probability of double  $\beta$ -transformation of two heavy particles.

We may notice here that there are also some other cases of isomeric nuclei indicating the presence of negative protons in the nuclear structure. To these belong the nucleus of  $UZ$  which seems to have the same charge and mass numbers as  $UX_2$  and also the stable isotope of lead  $^{210}_{82}\text{Pb}$  found by Aston which is isomeric with  $\beta$ -active  $\text{RaD}$ .

Turning our attention to the problems of  $\beta$ -disintegration we must consider the emission of a (negative or positive) electron from the nucleus as a result of the transformation of a nuclear neutron into a proton or conversely. If the above-mentioned negative protons do exist in the nuclei, certain  $\beta$ -transformations could be due to the transformation of a neutron into a negative proton or the reverse process. Thus for example the two kinds of  $\beta$ -decay of  $UX_1$ , leading to the nuclei  $UX_2$  and  $UZ$ , can be considered as due to transformations

$$n \rightarrow p^+ + e^- \text{ and } p^- \rightarrow n + e^-.$$

There is at present no consistent theory of the  $\beta$ -transformations of heavy particles as this question is evidently connected with the problem of elementary particles which is beyond the limits of the present quantum theory. Fermi has recently proposed a tentative theory of  $\beta$ -decay which is in fairly good agreement with experimental evidence. In this theory, however, the interaction energy between heavy and light particles is introduced purely phenomenologically and its absolute value is chosen so as to fit with the observed decay periods of  $\beta$ -active bodies. We cannot at present give any physical interpretation of these forces as they are too weak to be considered as electromagnetic but too strong to be connected with gravitational phenomena. Whatever the theory of  $\beta$ -transformations may ultimately be, it seems that, as far as questions of stability are concerned, it is possible to apply to  $\beta$ -transformations the same stability criteria as in the case of heavy particles: the transformation is energetically possible if the total mass of particles (heavy and light) resulting from the transformation is smaller than the mass of the particles entering the reaction. The mass difference will figure as the kinetic energy of the resulting particles, so that the law of conservation of energy will hold if we consider only the upper limits of the continuous energy distributions for light particles.

Accepting this proposition, we can draw certain conclusions about the  $\beta$ -stability limits of different nuclei as was done by Heisenberg in his general survey of nuclear stability.

Just as in the case of  $\alpha$ -disintegration, we can write the stability condition for  $\beta^-$ -disintegration in the form

$$\frac{\Delta E}{\Delta n_1} + \frac{\Delta E}{\Delta n_2} < \Delta M_n \quad \dots\dots(5),$$

where  $\Delta M_n$  is the mass-defect of the neutron constructed from a proton and a negative electron.

The condition for the stability relative to  $\beta^+$ -disintegration is

$$\frac{\Delta E}{\Delta n_2} + \frac{\Delta E}{\Delta n_1} < \Delta M_p \cdot c^2 \quad \dots\dots(6),$$

where  $\Delta M_p$  is the mass-defect of the proton as built up from a neutron and a positive electron.

From (5) and (6) we can conclude that the nucleus will be stable relative to electron emission only if

$$-\Delta M_p \cdot c^2 < -\frac{\Delta E}{\Delta n_1} + \frac{\Delta E}{\Delta n_2} < \Delta M_n \cdot c^2 \quad \dots\dots(7).$$

In the plot of  $n_1/n_2$  against  $n_1 + n_2$  (i.e.  $(A - Z)/Z$  against  $A$ ) the condition (7) represents a very narrow band, and if we plot the points corresponding to different known nuclei they will be dispersed in much broader regions. The explanation of this discrepancy can be found if we consider more in detail the binding energies of different isobaric nuclei. The important factor here is that by change of atomic number by two units (two protons converted into neutrons or the reverse process) a new nuclear  $\alpha$ -particle is formed (or split) with the consequence that with increasing atomic number, the binding energy of isobaric nuclei changes alternately by small and large steps. The binding energies of even-charged nuclei are located (for a given atomic weight) on a lower curve than those for odd-charged nuclei. This explains, for example, why in the region of radioactive nuclei the first  $\beta$ -decay always shows smaller energy than the second one. For lighter elements this difference between the first and second electron becomes much larger and we can expect cases where the emission of the first electron will be connected with a negative energy balance.

In such cases only the simultaneous emission of two electrons would be energetically possible, but the theory teaches us that the probability of such double disintegration (simultaneous transformation of two neutrons into two protons) is so very small that the elements in question can be considered as practically stable. Thus we come to the conclusion that isobars differing by two units in atomic number may exist in a practically stable state; which is in complete agreement with experimental evidence. We must not forget, however, that this stability is not an absolute one but means only very long periods of life.

A more detailed survey of the stability region for  $\beta$ -decay was made by the author using our present knowledge of the different isotopes. If we consider the total binding energy  $E$  of the nucleus as a function of  $n_1/n_2$  and  $n_1 + n_2$  it will be represented by a definite surface sloping towards the larger values of  $n_1 + n_2$ .

The cross-section of this surface in the direction  $n_1 + n_2 = \text{const.}$  will evidently represent the energy curve for nuclei of a given atomic weight which, according to the above considerations, must have a minimum for certain values of  $n_1/n_2$  somewhere between the two corresponding stable isobars.

In figure 1 is given a plot of the nuclei with even atomic weight, the isobaric nuclei being connected by vertical lines. It can be seen at once that no smooth curve can be drawn through the "doors" defined by isobaric nuclei. The curve representing the minima of binding energy (for  $n_1 + n_2 = \text{const.}$ ) has a wavy shape showing about eight minima. For the elements of odd atomic weight this curve has the same shape and practically coincides with the curve for even ones.

Some interesting consequences concerning the energies of  $\alpha$ -disintegration can be drawn from this curve. The region around the curve represents, so to speak, the valley on the binding energy surface. We must suppose that the energy conditions are especially favourable for  $\alpha$ -disintegration if it brings the point on our diagram into the valley. It can easily be seen from the figure that the conditions are especially favourable for the nuclei of ThC', RaC' and AcC' which, in fact, are known as possessing extremely high energy of  $\alpha$ -particles. It may be noticed also that the natural  $\alpha$ -activity of samarium may be connected with the

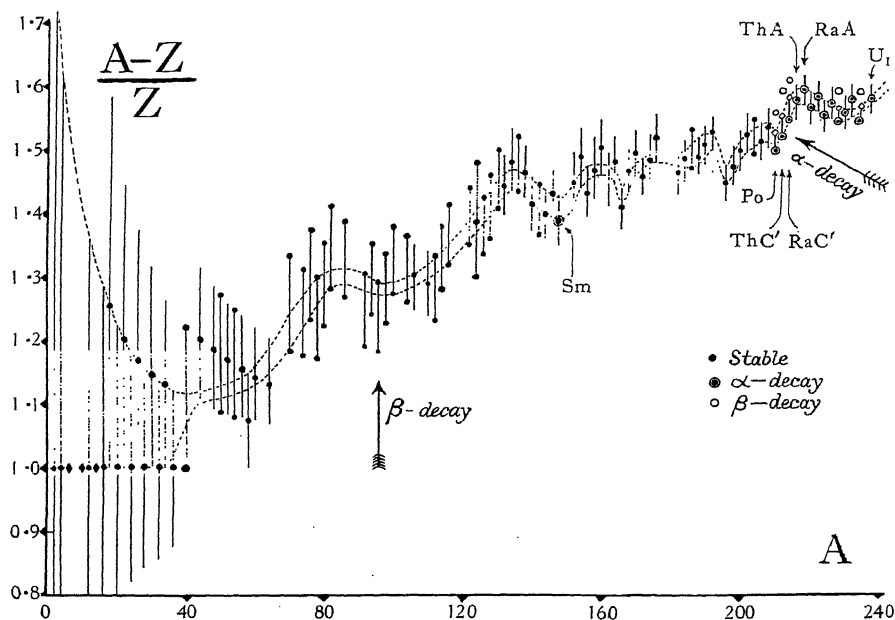


Figure 1.

favourable position of the corresponding point in relation to the valley of the binding energy surface.

The above considerations show that there exists a certain periodicity in the nuclear structure, most probably connected with the formation of saturated neutron shells. Traces of such periodicity may also be noticed in the mass-defect curve, as indicated by Landé, although in this case the experimental data on mass-defects are not precise enough to make it certain.

Again, the variation of nuclear radii gives some indication concerning the periodic properties of nuclei: the radii of different members of radioactive families, estimated from the rate of  $\alpha$ -disintegration, decrease too rapidly with atomic weight, so that it is impossible to continue this curve smoothly up to the light elements. Unfortunately we have at present no data for estimating the radii of nuclear potential barriers



in the whole region between radioactive elements and the lightest elements subject to artificial disintegration. On the other hand the nuclear collision radii of neutrons, as estimated by Dunning, show a regular variation through the whole region of the periodic system.

This can perhaps be understood on the basis of the hypothesis that the neutron scattering gives us the (uniformly varying) radii of the  $\alpha$ -particle aggregates in the nucleus, whilst the internal limit of the potential barrier is connected with the volume occupied by the neutronic shells.

## DISCUSSION

Dr H. A. BETHE. Dr Peierls and I have considered alternative forms for the Hamiltonian governing the  $\beta$ -decay which might replace the one suggested by Fermi and perhaps fit better with the observed energy distribution of the  $\beta$ -rays. Especially the absence of slow positrons found by Ellis for  $P_{18}^{30}$  should be accounted for. The difficulty is, however, that too many expressions for the Hamiltonian suggest themselves. A Hamiltonian in which the wave functions of electron and neutrino are either differentiated or multiplied by a spin matrix would, at least, give a smaller relative probability for the emission of slow electrons. But it may well be that an asymmetry between positron and negatron emission has also to be introduced.

There is a second argument in favour of the introduction of derivatives into Fermi's Hamiltonian. Heisenberg has suggested that the exchange forces assumed to act between neutron and proton in the nucleus are connected with the "Fermi field" of  $\beta$ -emission in the same way as the Coulomb interaction between charged particles is connected with the radiation field. This idea can only be carried through if it is assumed that the law of the Fermi field breaks down for very short distances of the order  $10^{-13}$  cm. With this assumption and Fermi's original Hamiltonian, the exchange forces turn out  $10^{12}$  times too small to account for the binding energies of nuclei, whereas one finds the right order of magnitude if one assumes the Hamiltonian for the  $\beta$ -decay to be of the form  $H = g \sum_{i=1}^4 \frac{\partial \psi}{\partial x_i} \frac{\partial \phi}{\partial x_i}$ ,  $\psi$  and  $\phi$  being the wave functions of electron and neutrino and  $g$  a constant.

Dr W. M. ELSASSER. The determination of the whole of the liberated energies in radioactive  $\beta$ -decay, which Dr Ellis has used for the construction of the nuclear level scheme, also serves for the calculation of another class of magnitudes important in nuclear structure. These are the binding energies of protons and neutrons, i.e. the energies which are liberated when a proton or a neutron, as the case may be, is added to the nucleus. The significance of these quantities for the theory of nuclear structure has been studied by Guggenheimer\*. Since even and odd nuclei cannot be directly compared, I confine myself to even nuclei, i.e. those of the radium and thorium series†. The energies of all the nuclei of one series are known relatively to

\* K. Guggenheimer, *J. de Phys.* 5, 253 (1934).

† W. M. Elsasser, *Comptes Rendus*, 199, 46 (1934).

each other. By the determination of an additive constant, the two series can be related to each other. It is then found that the constant can be chosen in such a way that the binding energies of all nuclei for which the proton number  $P \geq 82$  and the neutron number  $N \geq 126$  vary steadily as a function of  $P$  and  $N$ . From the numerical values  $W$  given in the table, the binding energy in m.e.v. of a *pair* of protons or neutrons is calculated by the formula

$$E = -931 (n - 1) - 6.24 + W,$$

where  $n$  is the mass of the neutron on the scale  $O^{18} = 16$ .

N	P					
	82	84	86	88	90	92
146						U <sub>1</sub> (4.0)
144					UX <sub>1</sub> (0.2)	...
142					4.3 Th 0.8	3.7 U <sub>11</sub>
140				MsTh <sub>1</sub> 0.4	4.0 Io	
138				Ra 1.24	3.5 RdTh	
136			Rn 0.60	4.28 ThX		
134		RaA 0.40	5.18 Tn			
132	RaB 0.11	6.00 ThA				
130	6.79 ThB 1.36	5.54 RaC'				
128	6.47 RaD 2.65	5.18 ThC'				
126	6.30 ThPb 3.98	4.97 Po				
124	1.42 RaPb					

A more exact analysis of the  $\alpha$ -decay energies including the odd nuclei shows that the straight lines  $P=82$  and  $N=126$  are *lines of discontinuity* in the  $P-N$  diagram; on them the binding energies experience a sudden jump. This phenomenon can be explained by the shell model of nuclear structure developed by Guggenheimer\* and myself† following a suggestion due to Bartlett‡.

Prof. E. FERMI. In connexion with the theory of  $\beta$ -rays I should like to point out that there is apparently some disagreement between theory and experiment as to the drop in intensity of the continuous  $\beta$  spectrum for low energies.

I do not think that experimental results are completely definite on this point, as the small penetrating power of low energy electrons greatly increases the difficulties

\* K. Guggenheimer, *J. de Phys.* 5, 253 (1934).

† W. M. Elsasser, *J. de Phys.* 5, 389 (1934).

‡ T. H. Bartlett, *Phys. Rev.* 41, 370 (1932) and 42, 147 (1932).

of investigating them; if however a disagreement should be established beyond doubt, it would still be possible to alter the particular form of interaction between protons and neutrons on one hand and electrons and neutrinos on the other, in order to re-establish the agreement. The form of this interaction that has been given in my theory of the  $\beta$ -rays was chosen only on account of its simplicity, but there is a large variety of other special forms for the interaction which might be tried if needed. This refers not only to the energy distribution in the continuous  $\beta$ -spectrum, but also to the selection rule of forbidden transitions, although the evidence which has been presented in Dr Ellis's report seems to be definitely in favour of the selection rule in its present form.

I heartily agree with Dr Gamow, that both his empirical evidence and the more general argument of symmetry strongly support the possibility of the existence of a negative proton. I should like nevertheless to point out some difficulties for his view-point, which are chiefly connected with the theoretical interpretation of the fact that the atomic weights are approximately equal to twice the atomic numbers. In Heisenberg's theory the interpretation of this fact is based on the simple assumption that the proton-neutron interaction is the main force in determining the nuclear binding, and is quite independent of more special assumptions on this interaction. If we now assume the existence inside the nucleus of a new kind of particle into which neutrons can transform with emission of a positive electron, it seems difficult to understand why the number of these negative protons always remains very small and is not noticeable in the relation of atomic weight to atomic number.

I agree with Dr Gamow that this difficulty is in no way a fundamental one, as one might assume that there are strong repulsive forces between protons of different signs, acting only at close distances; but if we assume these forces, it seems to me that they must be very delicately adjusted in order to prevent the formation of negative protons in considerable number, and yet to allow for their presence in nuclei of very different atomic weights, as beryllium and lead.

Dr H. O. W. RICHARDSON. Results have been obtained which suggest that the assumption that Radium E emits very few low-energy electrons is incorrect. Sources of Radium E were mounted on thin metal leaf in an expansion chamber and an unexpectedly large number of electrons with energies between 10 and 65 kV. was found, indicating that the height of the ordinate of the energy distribution curve in this region is of the same order as at the well-known maximum at about 350 kV. Presumably the curve drops considerably between this maximum and the 65 kV. which marked the highest energy investigated in these experiments, which therefore indicate a group of low-energy rays which is not explained by the present theories of  $\beta$ -decay.

Prof. K. SITTE: 1. An essential assumption of Fermi's theory is that those transitions which are accompanied by a change of nuclear spin of amount  $\Delta i$  ( $\neq 0$ )—"the forbidden transitions"—occur more rarely than the "permissible transitions," the ratio of occurrences being  $\left(\frac{\rho}{\lambda}\right)^{2|\Delta i|} \left(\frac{1}{100}\right)^{|\Delta i|}$ . It is known that, e.g. in the

case  $\Delta i = 1$ , the shape of the distribution curve as well as the value of the disintegration constant are influenced by the transitions of the  $s$ -electrons only, so that it is easy to put the above assumption to the test. For this purpose, it is only necessary to calculate the ratios of the probabilities of the transitions which, in our notation, are denoted by  $s_{\frac{1}{2}} - \pi_{\frac{3}{2}}$  and  $p_{\frac{1}{2}} - \sigma_{\frac{3}{2}}$  respectively to the probability of the transition  $s_{\frac{1}{2}} - \sigma_{\frac{1}{2}}$ , which is the deciding factor in the case when  $\Delta i = 0$ .

Using Fermi's eigenfunction, we find approximately, for heavy elements ( $Z/137 = 0.6$ ),

$$\frac{I_{+1-1}}{I_{-1-1}} = \frac{0.36 \left( \frac{W}{mc^2} - 1 \right) + 0.04 \left( \frac{W}{mc^2} + 1 \right)}{0.36 \left( \frac{W}{mc^2} - 1 \right) + 3.2 \left( \frac{W}{mc^2} + 1 \right)}$$

and

$$\frac{I_{-1}}{I_{-1-1}} = \frac{0.36 \left( \frac{W}{mc^2} + 1 \right) + 0.04 \left( \frac{W}{mc^2} - 1 \right)}{0.36 \left( \frac{W}{mc^2} - 1 \right) + 3.2 \left( \frac{W}{mc^2} + 1 \right)}$$

This ratio therefore depends in part on the energy of the electrons leaving the nucleus, and it is only in the first case, and for the slowest particles, that it reaches the value  $1/100$  assumed by Fermi. But it increases rapidly with the energy of the emitted particle, and in the second case it is never smaller than  $1/10$ , even for the slowest electrons.

Thus it is seen that neither is the shape of the distribution curve in the region of low energies so greatly altered, nor is the value of the disintegration constant so considerably reduced, as Fermi assumes.

Analogous calculations for the three transformations which are characteristic of the case  $\Delta i = 2$  show that there also the differences from the case  $\Delta i = 0$  are not large enough; it would consequently be necessary to insert yet higher values for  $\Delta i$ .

2. Again, the validity of any theory of  $\beta$ -disintegration can be tested by using in the formulae the constants obtained from a study of the natural radioactivity of heavy elements, when applying these formulae to the artificial  $\beta$ -disintegration of light elements. As the nature of the phenomena is the same in the two cases, it is reasonable to expect the theory to yield values of the disintegration constants which are at least of the same order of magnitude as the values determined experimentally, with plausible assumptions for the  $\Delta i$  of Fermi or for the quantum numbers  $j$  and  $j'$  of our notation. Unfortunately, none of the existing theories as at present developed fulfils this requirement.

The curves of figures 1 and 2 are drawn from the formulae of Beck and Sitte. Figure 1 gives the distribution curves for the emission of positrons with a maximum energy of 2 million electron-volts and quantum numbers  $j = 1, 2, 3$ . In this respect there is still good agreement between experiment and theory. Theoretical considerations lead us to expect only very few slow particles, and experiment shows, according to Ellis, that there are practically no positrons of less than 200,000 electron-volts.

There is no agreement, however, between the theoretical and experimental

values of the disintegration constants. Figure 2 gives a few  $\lambda - E_{\max}$  diagrams, the so-called "Sargent curves," for the quantum numbers  $j=1, 2, 3$ . It is seen that all the experimental values, with the exception of the very inaccurate measurements for  $^{23}_{11}\text{Na}$  and  $^8_5\text{B}$  (points 4 and 5 of figure 2b) are considerably lower than the values given by the theoretical curves corresponding to the same quantum numbers. It would therefore be necessary to use higher quantum numbers in order to explain

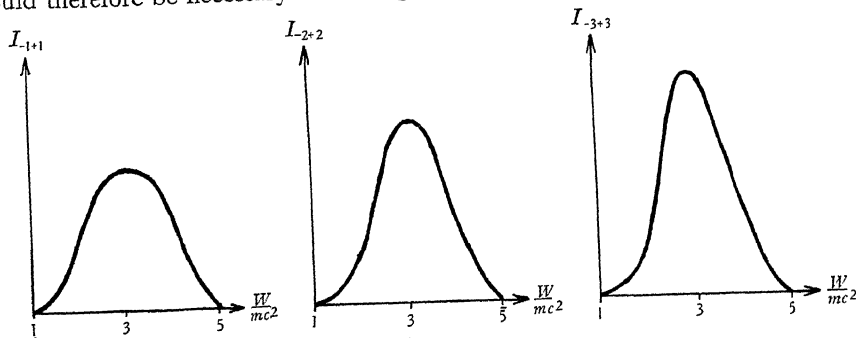


Figure 1.

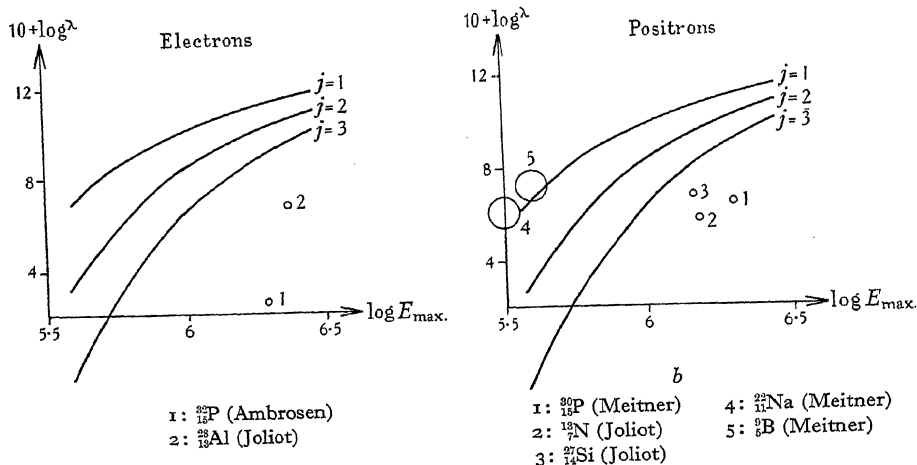


Figure 2.

the results of those low values; but that would be a very unreasonable assumption, for already  $j=2$  and  $3$  were found to be adequate for the heavy elements, and rather lower values would be expected for the lighter elements.

Fermi's theory is subject to the same discrepancies, and shows a similar want of agreement between the theoretical and experimental values of the disintegration constant. Moreover, the distribution curves of the emitted particles in the region of small energies fall more slowly according to Fermi's theory than according to ours. Experiments hitherto performed therefore provide no support for Fermi's theory.

It appears then that the phenomenon of  $\beta$ -ray disintegration is still far from being thoroughly understood, and it seems premature to build up a theory requiring such special assumptions as Fermi's. We must for the present be content with a much more general description of the phenomena like that previously given by Beck and Sitte. That such a general description can account for a number of new results on the properties of the nucleus is again proved in Beck's paper, where it is shown that by simply regarding  $\beta$ -ray disintegration as a double process, it is possible—even without making any assumption about the second particle emitted along with the electron—to deduce our selection rule for the emitted charges. Further, in a general theory of this kind, the insufficient agreement between experimental and theoretical values of the decay constants must not be regarded as an essential failure, but only as implying incompleteness of the theory, and this may give rise to further studies on the variation of the constants with atomic number.



# ARTIFICIAL RADIOACTIVITY





## ARTIFICIAL RADIOACTIVITY PRODUCED BY NEUTRON BOMBARDMENT

By E. FERMI

Rome

*ABSTRACT.* The advantages of neutrons as bombarding particles are pointed out, and experiments are described in which radioactive elements are produced by this process. About 40 cases were found, out of 60 examined.

In general, the atomic number of the radioelement formed is either that of the parent element, or is less than this by either 1 or 2 units, the first case being commonest among the heavier elements.

It is assumed that the first stage is the capture of the neutron, and that this is followed by the ejection of a quantum of  $\gamma$ -radiation, a proton or an  $\alpha$ -particle. The first stage presents no theoretical difficulty, but the subsequent ejection is not easy to understand. The theoretical difficulties presented here are briefly discussed.

AFTER the discovery by Mons. and Mme Joliot that radioactive substances could be obtained by bombardment with  $\alpha$ -particles, I undertook experiments in the Physical Institute of the University of Rome to investigate whether phenomena analogous to those observed by the Joliot's could also be obtained as a result of neutron bombardment. Although the neutron sources which it is possible to employ are inferior to the sources of  $\alpha$ -particles or of swift protons, yet right from the beginning we could expect a certain compensation owing to the fact that neutrons, being uncharged, are more efficient in producing artificial disintegrations than charged particles; in particular we could hope for results even in the case of heavy atoms which up to the present have been unaffected by bombardment with charged particles.

Experience has fully confirmed these expectations, neutron bombardment having given rise to the formation of radioactive products in about 40 cases (out of 60 elements studied up to the present). This high fraction of elements which can be activated is very roughly the same for light elements as for heavy ones.

Without describing in detail the results obtained to date, which have been published\*, I must give a little space to certain problems relating to the interpretation of the results themselves.

One of the points of greatest interest is that of ascertaining what is the nuclear reaction which gives rise to the formation of the radio-element obtained by bombarding a given element of atomic number  $Z$  with neutrons. An important factor

\* For a résumé of this work see Fermi, Amaldi, D'Agostino, Rasetti and Segrè, *Proc. Roy. Soc. A*, 146, 483 (1934).

in discussing this question is the chemical examination of the radioactive element, an examination which it has been possible to carry out in a fairly large number of cases. The result has been to show that the atomic number of the element formed may be (except for the case of uranium, where probably several successive transformations are involved) one of the following:  $Z-2$ ,  $Z-1$ ,  $Z$ .

The first two cases are common among the light elements, whilst for heavy elements only the last case has been encountered up to the present.

In interpreting these facts we may assume that the process of formation of radio-elements consists in the absorption of neutrons by the bombarded nucleus, with the emission either of an  $\alpha$ -particle (radio-element with atomic number  $Z-2$ ) or a proton (radio-element with atomic number  $Z-1$ ) or a quantum of  $\gamma$ -radiation, necessary because the neutron loses its initial energy (radio-element of atomic number  $Z$ ). In the cases examined up to now, this hypothesis is compatible with the facts; in particular, if the atomic weight of the radioactive isotope which would be formed by the bombardment is calculated on this hypothesis, it never corresponds to that of a known stable isotope; further, whenever on the basis of these three possible processes, it is found that isotopic isobars should be obtained by bombardment of different elements, then they are actually found to have the same mean life, which confirms that the same radioactive element is in this case obtained in different ways.

Turning now to the consideration of these processes from the point of view of present theories of nuclear structure, it appears that there is no theoretical difficulty in understanding how it may happen that the neutron is captured in a large percentage of cases with the expulsion of an  $\alpha$ -particle or a proton; remembering that these particles, in order to escape from the atom, must penetrate Gamow's potential barrier, it is found, in agreement with experiment, that the probability of processes of this kind decreases fairly rapidly with increasing atomic number of the bombarded element; in such a way that unless we accept rather unlikely values for the energy of the emitted  $\alpha$ -particle or proton, the process would become practically impossible for the heavy elements. On the other hand, there are considerable theoretical difficulties in understanding the simple capture of the neutron, which would lead to the formation of a radio-element isotopic with the original element but with an atomic weight greater by unity. As a matter of fact, in this case the neutron at the moment of capture has an energy surplus equal to its kinetic energy, i.e. several millions of electron volts. In this condition, the neutron would escape from the nucleus in an extremely short time which, if we accept the usual views on nuclear structure, would be of the order of  $10^{-20}$  or  $10^{-21}$  sec.; to ensure the capture of the neutron a quantum of  $\gamma$ -radiation of sufficient frequency to carry off the excess energy of the neutron must be emitted in this short interval of time, so that the probability of simple capture of the neutron would equal the probability of emission of the quantum of  $\gamma$ -radiation in a time interval of the order mentioned. If we accept the usual data for the probability of emission of  $\gamma$ -radiation by an excited nucleus, the calculated probability comes out much less than that observed. If we wish to retain the hypothesis of the possibility of this process of neutron capture, we

must admit that for some reason which we do not know the neutron can remain in the excited nucleus for a much longer time than that quoted; or else the process of expelling the excess energy, either by the emission of a quantum of  $\gamma$ -radiation or by some other unknown process, can occur much more rapidly. In view of this position of the theory, the observations of Bjerger and Waiscott on the activation of sodium, and those of Amaldi and Segrè on aluminium, are to be considered particularly important; they seem to prove that, at least in one of the processes of activation, a radioactive isotope of the same element is formed, having an atomic weight increased by one unit. Finally we must note that completely analogous difficulties of interpretation to those just discussed present themselves in the explanation of the synthesis of heavy hydrogen observed by Lea when hydrogen is bombarded with neutrons.

## ARTIFICIALLY PRODUCED RADIO-ELEMENTS

BY MONS. AND MME JOLIOU

Paris

*ABSTRACT.* After a general survey of the nature of nuclear reactions, the case where aluminium is bombarded by  $\alpha$ -particles from polonium is dealt with. Here positive electrons are emitted as well as other products, but with the peculiarity that the emission only commences after several minutes of irradiation whilst it continues for a time after the cessation of the bombardment. In fact, the radiation decays with a half-period of  $3\frac{1}{4}$  min. Boron and magnesium show a similar phenomenon, with a different rate of decay.

It is clear that a new type of radioactivity is present, which might be due either to the formation of unstable isotopes or of known isotopes in an excited state. Reasons are given for preferring the former hypothesis. In each case it is supposed that the radioactive nucleus has a charge greater by 2 units, and a mass greater by 3 units, than the parent nucleus. These nuclei then disintegrate to give a positive electron, leaving an atom of the next element in the periodic table.

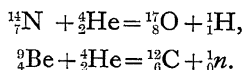
The hypothesis has been tested by examining the chemical nature of the radioactive element, and is found to agree with the facts.

From the fact that, for example, the nucleus  $^{10}_5\text{B}$  can be transformed into  $^{13}_6\text{C}$  by either of two processes, only one of which involves the emission of a neutron, it is possible to calculate the mass of the latter from the energy relations (assuming that the internal energy of the  $^{13}_6\text{C}$  nucleus is the same in both cases). The result from boron is 1.0098, and from aluminium there is a less reliable value of 1.0092. It is suggested that the value 1.010 be adopted. This suggests that the neutron is unstable and should break up into a proton and a negative electron.

The paper concludes with a discussion of the various experimental results of other cases of artificial radioactivity produced by bombardment either with  $\alpha$ -particles or neutrons.

THE various types of transmutation phenomena which have been discovered recently have all received a common interpretation, similar to that accepted for the transmutation of nitrogen under the action of  $\alpha$ -rays: a particle ( $\alpha$ -ray, proton, deuteron or neutron) enters a nucleus; the nucleus disintegrates and expels a particle differing from the original one.

Thus we have, for example:

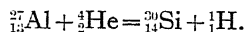


It was supposed that the reaction would leave a stable nucleus as residue, and, as a matter of fact, the main reactions interpreted in this manner lead to the formation of a known nucleus, although occasionally this may be a very rare isotope like  $^{17}_8\text{O}$  or  $^{13}_6\text{C}$ .

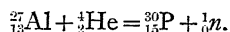
It is known that the nuclei of fluorine  ${}^{19}_9\text{F}$ , of sodium  ${}^{23}_{11}\text{Na}$  and of aluminium  ${}^{27}_{13}\text{Al}$  emit protons on transmutation under the action of  $\alpha$ -rays. We have shown that these same nuclei also emit neutrons under the action of  $\alpha$ -rays.

Although the interpretation of the emission of protons is simple, and leads to the formation of a stable nucleus, the setting-up of a formula for the nuclear reaction to explain the emission of neutrons meets an unexpected difficulty.

For example, in the case of aluminium, the nuclear reaction accepted for the emission of protons is



A similar formula for the emission of neutrons gives



Whilst the first reaction results in the formation of a known stable nucleus,  ${}^{30}_{14}\text{Si}$ , the second reaction leads to an unknown phosphorus of mass 30. We shall see later how this anomaly, which at first gave us considerable food for thought, assumed its true significance after the discovery of the new radioactive elements.

## § 1. POSITIVE ELECTRONS FROM TRANSMUTATIONS

The known transmutations of various types take place with the emission of protons, neutrons and  $\alpha$ -rays. The emission of electrons in the course of these nuclear disintegrations had never been observed.

We have observed the radiation emitted by a polonium source covered with a thin sheet of aluminium foil, by means of a Wilson expansion chamber. The source was placed outside the apparatus, opposite an orifice in the wall of the expansion chamber formed by a thin covering. A magnetic field deflected the electrons and permitted their energy to be measured.

We observed the emission, not only of protons from the transmutation of aluminium, but also of numerous positive and negative electrons. The negative electrons, whose energy does not in general exceed  $0.9 \times 10^6$  e.V., can be attributed to the internal conversion of the  $\gamma$ -rays of polonium; they are also observed when the polonium source is covered with a thin sheet of silver. The positive electrons have a higher mean energy, reaching  $3 \times 10^6$  e.V., and they certainly originate in the aluminium. Their number is of the order of  $10^{-6}$  times the number of  $\alpha$ -particles, which corresponds well to a transmutation phenomenon.

Positive electrons are also observed when the polonium source is covered with a thin layer of boron or beryllium; in the latter case, there is also an emission of negative electrons of several million electron volts energy.

It is known that under the action of  $\alpha$ -rays beryllium emits a radiation of neutrons and a  $\gamma$ -radiation of quantum energy  $5 \times 10^6$  e.V. We attribute the emission of negative and positive electrons in this case to an "internal materialization" of the  $\gamma$ -radiation; the  $\gamma$ -radiation being transformed into a positive and a negative electron in the process of leaving the nucleus which gave rise to it.

This explanation can in no way suit the case when positive electrons are emitted by aluminium; on the one hand, as far as is known, no  $\gamma$ -radiation of sufficient energy

is excited in aluminium; on the other hand, no negative electrons which could be attributed to such a materialization phenomenon are observed.

In this case, we have put forward the following interpretation: When an  $\alpha$ -particle is captured by a  $^{25}_{13}\text{Al}$  nucleus, there can be emission, either of a proton, or of a neutron and a positive electron; the nucleus which results from the transmutation is, in both cases, the stable nucleus  $^{30}_{14}\text{Si}$ . This interpretation gets rid of the difficulty which was encountered in explaining the emission of neutrons by aluminium.

We may suppose that the emission of neutrons by fluorine or sodium could be explained in the same way. Again for boron, the emission of neutrons would be attributed, not to the isotope  $^{11}_5\text{B}$  as was at first supposed, but to the isotope  $^{10}_5\text{B}$ , which emits protons on transmutation.

## § 2. DISCOVERY OF NEW RADIOACTIVE ELEMENTS, EMITTERS OF POSITIVE OR NEGATIVE ELECTRONS

In the course of experiments carried out to determine the minimum energy of  $\alpha$ -rays which would produce positrons from aluminium, we noticed that their emission is not instantaneous, but that *it is only produced after several minutes of irradiation, and continues for a short time after the cessation of the irradiation.*

Let a piece of aluminium foil be irradiated with the  $\alpha$ -rays from a strong polonium source for a few minutes; when the foil is withdrawn, it possesses an activity which decreases by half in 3 min. 15 sec.; the radiation emitted, which can be observed by means of a counter or a Wilson apparatus, consists of positive electrons.

Irradiated boron and magnesium also exhibit a lasting radioactivity, of periods 14 and  $2\frac{1}{2}$  min. respectively. The decay of the activity follows an exponential law.

We are then definitely confronted by new radio-elements, and by a new type of radioactivity, with the emission of positive electrons.

The initial intensity of the radiation observed increases with the time of irradiation  $t$ , up to a limiting value  $I_\infty$ , following a law  $I = I_\infty (1 - e^{-\lambda t})^*$ , as, for example, in the case of the accumulation of radon in radium. The limiting activity is practically attained after a time equal to a few periods of the radioactive body formed (about a quarter of an hour for aluminium, and an hour for boron).

The energy of the  $\alpha$ -rays from the source of irradiation does not seem to affect the period or the energy of the radiation from the radioactive body formed. If the energy of the  $\alpha$ -rays is too small, the phenomenon does not occur.

When aluminium and boron are irradiated, only positive electrons are observed. If any negative electrons exist, they are less numerous, or their energy is below  $2 \times 10^5$  e.V. Magnesium, on the other hand, emits negative and positive electrons; the former are more numerous and have the greater energy.

For aluminium, the upper limit of the energy of the positrons is  $3 \times 10^6$  e.V., and the most probable energy is  $1.0 \times 10^6$  e.V., a result agreeing with our first experiments on transmutation electrons. The lower limit is uncertain, because very slow electrons would not be observed, but it is certainly below  $2 \times 10^5$  e.V. For boron,

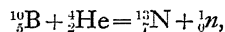
\*  $\lambda$  is the disintegration constant of the radio-element formed.

the upper limit of energy is  $1.5 \times 10^6$  e.V., and the most probable energy is  $0.5 \times 10^6$  e.V. Irradiated magnesium gives a continuous spectrum of negative electrons of maximum energy  $2.2 \times 10^6$  e.V., the most probable energy being  $0.7 \times 10^6$  e.V., and a continuous spectrum of positrons of maximum energy  $1.5 \times 10^6$  e.V. The distribution of the electrons in a continuous spectrum confirms us in the idea that the radioactive bodies produced are quite analogous to the natural radio-elements.

On the nature of the elements formed, two hypotheses can be put forward: the active nuclei are unstable isotopes of certain light elements, or else known stable nuclei, formed in a particular excited state. The first hypothesis seems to us the more probable.

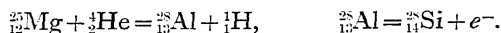
The following are the nuclear reactions that we accept, in agreement with our former interpretation of the positive electrons from transmutations.

The nuclei  $^{10}_5\text{B}$ ,  $^{24}_{12}\text{Mg}$  and  $^{27}_{13}\text{Al}$  undergo transmutation, with capture of the  $\alpha$ -particle, and emission of a neutron, yielding the unknown nuclei  $^{13}_7\text{N}$ ,  $^{27}_{14}\text{Si}$  and  $^{30}_{15}\text{P}$ . These are unstable nuclei which disintegrate with the emission of positrons to form the stable nuclei  $^{13}_6\text{C}$ ,  $^{27}_{13}\text{Al}$  and  $^{30}_{14}\text{Si}$ . Taking, for example, the case of boron, we have



followed by  $^{13}_7\text{N} = ^{13}_6\text{C} + e^+ + m$  ( $m$  = antineutrino).

The negative electrons of magnesium are probably emitted by a nucleus  $^{25}_{12}\text{Al}$  formed from the isotope  $^{24}_{12}\text{Mg}$  by capture of the  $\alpha$ -particle and emission of a proton.



The negative electrons being about four times as numerous as the positive electrons, the period of 2 min. 15 sec. observed for irradiated magnesium is that which corresponds to the radio-element emitting  $\beta$ -rays. We have not yet determined the period of the element emitting positrons.

### § 3. CHEMICAL TEST OF THE TRANSMUTATIONS

Phenomena of artificial transmutation present themselves to the physicist with a character of certainty. The physical experiments have proved the existence of these phenomena, and have even sufficed for the definite conclusion that the particles which produce the transmutation are captured in the nucleus, just as the experiments of Blackett originally showed in the case of the transmutation of nitrogen with the emission of a proton under the action of  $\alpha$ -rays.

However, it has never been possible to verify the reality of the transmutations by chemical methods, as in the case of the natural disintegration of radioactive elements. This is due to the fact that the number of stable atoms produced by these artificial transmutations is too small to be revealed by any method of analysis and, consequently, the chemical properties of these atoms cannot be recognized.

On the other hand, when the elements obtained by transmutation are radioactive, they can be identified by their radiation, even if the number of atoms is very small.



We decided to check the hypotheses that we had made on the nature of these elements by determining their chemical type.

*Transmutation of boron.* Boron, consisting of hard chemically resistant grains, does not lend itself well to these experiments. We irradiated boron nitride (the nitrogen produces no effect with the  $\alpha$ -rays from polonium). Boron nitride, BN, is decomposed by hot alkali, and the nitrogen liberated in the form of ammonia. This operation can be carried out in a few minutes. It is found that the boron loses its activity. The ammonia liberated is collected in a thin-walled tube, and its activity measured by means of an ionization chamber, closed by a thin sheet of aluminium, and connected to a Hoffmann electrometer. When allowance is made for the decrease of activity during the manipulation, it is found that the greater part of the activity is located in the tube. The radio-element has then the chemical properties of nitrogen; it is liberated in the form of nitrogen or of ammonia, carried along by the inert ammonia.

*Transmutation of aluminium.* A thin sheet of irradiated aluminium is dissolved in HCl. The aluminium salt, dried immediately, is almost completely inactive. The hydrogen liberated can be collected in a thin-walled tube, and it is found that it carries the activity with it. It is necessary to work very quickly, on account of the rapid decay of the activity; the operation can be carried out in 3 min.

The radio-element, which should have the properties of phosphorus, must have originally been in the gaseous state in the form of hydrogen phosphide produced by the nascent hydrogen. If the aluminium is dissolved in the oxidizing medium  $\text{HCl} + \text{HNO}_3$  the activity remains with the aluminium.

The latter reaction would proceed similarly if the radio-element had the properties of silicon, since, in this case, hydrogen silicide would be formed.

We may also dissolve the irradiated aluminium, add sodium phosphate, and precipitate by a zirconium salt. The zirconium phosphate which is precipitated in slightly acid solution carries down the activity with it. It is thus probable that we are really dealing with an isotope of phosphorus.

The above chemical experiments give a chemical proof (1) that the element formed by transmutation is different from the original element, and (2) that the  $\alpha$ -particle is captured in the nucleus.

We propose to call the new radio-elements emitting positrons or  $\beta$ -rays, and produced by the action of  $\alpha$ -rays on boron, magnesium and aluminium, *radio-nitrogen*, *radio-aluminium*, *radio-silicon* and *radio-phosphorus*.

Similar nomenclature could be adopted in the case of other new radio-elements. Nevertheless, more than one active isotope of a given element can exist. A convenient nomenclature could hardly be established before we know better what cases can occur.

#### § 4. MASS OF THE NEUTRON

It may be assumed, as in the case of the continuous spectrum of  $\beta$ -rays, that the emission of each positron emitted by a radio-element is accompanied by that of a "neutrino," or maybe, in this case, of one of Louis de Broglie's "antineutrinos,"

whose energy is complementary to that of the electron. The existence of such a particle is suggested, not only by the law of conservation of energy, but also by that of conservation of spin.

The energy of disintegration in this case would be the maximum energy of the positron spectrum.

The transformation of the nucleus  $^{10}_5\text{B}$  into a  $^{10}_6\text{C}$  nucleus can occur either with the emission of a proton, or with emission of a neutron followed by a positive electron. The same thing applies to the transformation from  $^{27}_{13}\text{Al}$  to  $^{27}_{14}\text{Si}$ .

If it is admitted that the two modes of transformation lead to exactly the same final nucleus, they should liberate the same energy. This permits us to calculate the mass of the neutron without needing to know the exact mass of any other nucleus than that of the proton. It is necessary to know, for a given energy of the exciting  $\alpha$ -rays, the maximum energy of the protons, the neutrons and the positive electrons.

From the transmutations of boron, the value  ${}^1_0n = 1.0098$  is calculated, whilst those of aluminium give  ${}^1_0n = 1.0092$ . The figures relating to boron being the more accurate, we can accept approximately  ${}^1_0n = 1.010$ , a value which is compatible with the stability of the beryllium nucleus.

Naturally, if the nuclear reactions were accompanied by the emission of  $\gamma$ -radiation, the mass calculated for the neutron would be modified. Again, the calculations are invalid if (as Pauli and Gamow have supposed) the two modes of transmutation do not lead to identical nuclei, but to isotopic isobars of different internal energy.

If the mass 1.010 is accepted for the neutron, then the transformation: proton  $\rightarrow$  neutron +  $e^+$  absorbs energy  $3.1 \times 10^6$  e.V., and the transformation: neutron  $\rightarrow$  proton +  $e^-$  liberates  $2 \times 10^6$  e.V.

If this is so, the neutron must be unstable and would be transformed spontaneously into proton +  $e^-$ . It is unfortunately rather difficult to check this experimentally owing to the great penetrating power of neutrons. Moreover, the neutron could combine with a positive electron, with the liberation of  $3 \times 10^6$  e.V.

The transformation proton  $\rightarrow$  neutron may perhaps be observed outside the nucleus, either at the moment of impact of a swift proton with a nucleus, or by bombarding hydrogen with particles capable of projecting protons with energy greater than  $3.1 \times 10^6$  e.V.

It may be expected that the emission of a proton will be replaced by that of a neutron and a positive electron, in nuclear transmutations, provided that the energy of the protons exceeds  $3.1 \times 10^6$  e.V.; this is not, however, a sufficient condition, since the maximum energy of the positive electron is determined by the radioactive properties of the intermediate nucleus formed, and it must furnish energy of at least  $3.1 \times 10^6$  e.V. +  $W_e$ .

## § 5. FURTHER EXPERIMENTS ON ARTIFICIAL RADIOACTIVITY

Following on our first experiments, we suggested that other radio-elements, unknown radioactive isotopes of stable bodies, would be obtained by the action of the various particles with which transmutations can be produced— $\alpha$ -rays, protons,

deutons, and neutrons. On the other hand, we might hope to form certain radioactive nuclei by several different nuclear reactions.

A number of experimenters have attacked this question and, in the course of three months, a number of new radio-elements have been discovered.

*Irradiation by  $\alpha$ -rays.* Ellis and W. J. Henderson\* have confirmed our results and observed a period of about 1 min., attributed to an impurity in the irradiated substance. Wertenstein† has shown that nitrogen, irradiated by  $\alpha$ -rays of 5 cm. range, gives a new radio-element of period 1.2 min. which can be deposited by recoil on the various irradiated elements. (This is probably the substance observed by the previous authors.) We also have observed this phenomenon of recoil of active nuclei. This radio-element is probably a nucleus  $^{19}\text{F}$ , emitting positrons. Nitrogen irradiated by  $\alpha$ -rays from polonium gives protons of  $3.4 \times 10^6$  e.V., but neither neutrons nor lasting radioactivity is observed. When the energy of the  $\alpha$ -rays is a little greater, the emission of the proton may be replaced by that of a neutron and a positron. This is in accordance with the views set out above: the replacement of the proton by a neutron +  $e$  takes place when the energy of the proton is  $3.1 \times 10^6$  e.V. + an energy which depends on the nucleus considered, and which must be given up to the positive electron.

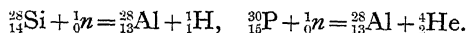
Frisch has shown that sodium and phosphorus irradiated by the  $\alpha$ -rays from the active deposit of thorium give radio-elements emitting positrons and having periods 7 sec. and 40 min. respectively.

Fluorine, which emits protons and neutrons under the action of  $\alpha$ -rays, probably gives a radio-element of even shorter period than does sodium. Mlle Meitner has recently announced the existence of a radio-element emitting positrons in lithium irradiated by  $\alpha$ -rays.

*Irradiation by neutrons.* We shall not speak here of the beautiful experiments carried out in England, the United States and Italy by means of protons, deutons and neutrons. They will be dealt with in other papers. We discuss solely some experiments which we have carried out by means of neutrons.

Irradiated silicon gives a radio-element of which the period of 2 min. 40 sec. is equal within the accuracy of the experiments (possible error about 20 sec.) to that of the radio-element emitting  $\beta$ -rays which is formed in irradiated magnesium. In the same way, with phosphorus irradiated by neutrons, a period of 2.5 to 3 min. is observed, in addition to a period of 3 hours. The maximum energy of the  $\beta$ -rays is practically the same in the three cases.

It is very probable that we are dealing with the same nucleus  $^{28}_{13}\text{Al}$ , see p. 81, formed from Si and from P by the reactions



Irradiated phosphorus and silicon placed near the thin window of the chamber of the Wilson apparatus show the emission of numerous negative electrons coming from the source, whose energy can reach about  $2.3 \times 10^6$  e.V., together with a few

\* Ellis and W. J. Henderson, *Nature*, **133**, 530 (1934).

† Wertenstein, *Nature*, **133**, 565 (1934).

positive electrons of smaller energy; on the other hand, we observe transverse electrons hardly deflected in the magnetic field of 900 gauss maintained in the expansion chamber: these electrons, of which the energy must reach at least  $7 \times 10^6$  e.V., probably prove the existence of  $\gamma$ -rays of large quantum energy, unless they are produced by some unknown secondary mechanism.

If it is indeed a question of  $\gamma$ -rays accompanying the emission of the disintegration  $\beta$ -rays from the radio-elements formed, then the total energy of disintegration is considerable—greater than the energy of any  $\gamma$ -ray at present known to be emitted by sources of terrestrial origin.

The emission of some positive electrons can be explained by a phenomenon of materialization of these  $\gamma$ -rays, that is by the production of a pair of positive and negative electrons by the radiation, either on leaving the nucleus which emits it, or else in the nuclei encountered later.

If, however, the emission of the positive electrons is due to the formation in small amounts of a radio-element emitting positrons under the action of neutrons, then it is very difficult to imagine what is the reaction. A possible interpretation would be to suppose that the entrance of the neutron into the nucleus is followed by the expulsion of a negative proton. The nucleus resulting from such a transformation could be a substance emitting positrons.

The expulsion of a negative proton would perhaps explain the formation of the substance of atomic number 93 obtained by irradiation of uranium with neutrons.

Certain experiments have led us to think that the bombardment of phosphorus by neutrons could produce radio-elements which themselves emit neutrons.

## § 6. CONCLUSIONS

We remark first of all that the terms “artificial radioactivity” or “induced radioactivity” frequently employed to designate the new phenomena are convenient but not very appropriate. As a matter of fact, one does not artificially render a nucleus radioactive, but transforms this nucleus into a different nucleus which is naturally unstable. Up to the present, all attempts made to alter the stability of atoms, whether in stable substances or in radioactive substances, have failed.

Seeing the rapidity with which so many new results have been obtained on artificial radioactivity, we can judge what developments will occur in this new field of study. We can hope from it a considerable extension of our knowledge of the physics of the nucleus.

In particular, it will be possible to settle a fundamental point: are the properties of the atom entirely determined by the mass and charge of the nucleus, or do isotopic isobars exist which possess different radioactive properties? Does one and the same nucleus formed by different nuclear reactions always present the same characteristics?

The results obtained are very much in favour of Heisenberg's view, according to which the elements which constitute the nucleus are protons and neutrons in proportions approximately fixed in each part of Mendeleieff's table. Actually, a nucleus

containing an excess of protons is destroyed by transformation of a proton into a neutron in the nucleus, and the expulsion of a positron; a nucleus containing an excess of neutrons is destroyed on the other hand by intranuclear transformation of a neutron into a proton, with the expulsion of a  $\beta$ -particle.

At the present time, it is certain that a great number of nuclei, isotopes of stable nuclei, are radioactive elements which do not exist in nature on account of their instability. The natural radio-elements now appear to us as rare survivors of numerous radio-elements which must have been formed at some time under different conditions of temperature, pressure, and radiation than those which have existed for millions of years on the terrestrial globe.

Future work will probably reveal to us new radioactive families, or unknown types of radioactivity with emission of protons, neutrons or other particles.

The energies and intensities at present obtained in the tubes for producing accelerated particles allow us to hope that soon we shall be able to produce, by means of these particles, radio-elements with an intensity of radiation comparable or even superior to that of preparations of natural radio-elements now available.

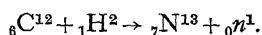
These radio-elements may be applied in medicine and perhaps in other practical fields. When introduced into the living body, these substances must behave very differently from ordinary radio-elements on account of their different chemical properties and because of their disintegration without leaving any radioactive residue.

Certain of the new radio-elements emit  $\gamma$ -rays by themselves. Moreover, those which emit positrons produce annihilation radiation of  $5 \times 10^5$  e.V. in great intensity in neighbouring matter, and consequently they act as sources of homogeneous  $\gamma$ -rays, and could be utilized to this end.

Finally, we must anticipate a considerable development in the use of these radioactive nuclei as indicators to study the behaviour of their inactive isotopes in certain chemical reactions or in biological phenomena.

## DISCUSSION

Dr J. D. COCKCROFT. I would like to draw attention to the very interesting result that we apparently have two kinds of radio-nitrogen; one formed by the bombardment of boron by  $\alpha$ -particles; the other by the bombardment of carbon by protons and deuterons. These two radioactive isotopes have apparently the same charge and mass but different decay periods and may, therefore, be examples of isomeric nuclei. M. Joliot has asked what the evidence is for the radioactive product obtained from carbon being nitrogen. Dr Walton and I have shown that the product is a gas which is not condensed by liquid nitrogen boiling at normal pressure but which is condensed when it is mixed with nitrogen and cooled by liquid air boiling at a pressure of 1 cm. We have also verified the ejection of a heavy particle in the primary reaction, which we assume to be



We have further shown that the activity is not due to impurities of lower atomic

number than fluorine and it seems unlikely that we could excite activity in elements of higher atomic number with our voltages.

I would like further to point out that the production of radioactivity in carbon by protons is another example of the capture process which Prof. Fermi has described for neutrons. In the former case there appears to be about one chance in a hundred thousand that capture will result after penetration of the nucleus.

Mlle Dr S. MARACINEANU. I should like to call attention to my investigations carried out since 1924 on the artificial radioactivity of metals\*. These were carried out firstly at the Radium Institute in Paris, then at the Observatories of Meudon and Paris, and later in Rumania.

My results have been published in various notes to the French and the Rumanian Academies of Science. The notes to the former were frequently accompanied by comments from M. H. Deslandres stressing the importance of the matter.

The investigations arose out of the anomalies in the decay constant of polonium, which have also been noticed by other workers†, and I arrived at the conclusion that the period varied with the metal support of the polonium‡.

After lengthy investigations, I found that the variation was due to excitation of the support by the  $\alpha$ -radiation from the polonium. Radioactivity was induced in the support, lead showing a stronger and more lasting effect than other metals (aluminium, copper, silver, gold, etc.). The radioactivity grew according to the exponential law characteristic of radioactive processes, the slight activity of the support causing the apparent constant of the polonium to vary. I also found that the  $\alpha$ -rays from polonium and solar radiation together exerted an action on the lead support. Finally, I noticed that the action of solar radiation was the perturbing cause in the radioactivity of uranium, and I explained the day-to-day variations in the radioactivity of uranium as pulsations due to the sun's activity, which itself varies from day to day. I was thus led to seek for radioactivity in old roofs, and I found among others that the lead roof of the Paris Observatory was radioactive. Lead taken from this roof does not lose its activity on thorough cleaning; even at a depth of several tenths of a millimetre and after ten years in the laboratory, it still retains a constant activity§, which cannot be ascribed to a deposit from the air: Ra D has  $T=16$  years.

Recently Steinke and Sweidler at Königsberg have found that lead becomes radioactive under the action of cosmic rays, and they determined the period as  $10^{27}$  years.

Lead must be feebly radioactive, as is proved by the mercury which exists as a permanent impurity in it; this feeble radioactivity is probably possessed by all bodies, and can be appreciably increased by artificial means.

Finally, I may remark that the effect of solar radiation on radioactivity has a

\* S. Maracineanu, *Bull. Acad. roumaine*, nos. 3-4 (1924); no. 6 (1929); no. 3 (1930); *Comptes Rendus*, 181, 774 (1925); 183, 345 (1926); 184, 1322, 1547 (1927); 185, 122 (1927); 187, 746 (1928).

† Rutherford, *Phil. Mag.* 10, 290 (1905); Mme Curie, *J. de Phys.* 12 (1920); Meyer and Sweidler, *Wien. Ber.* 115, 63 (1906); Markwald and Greinacher, *Jahrb. d. Radioakt.* 2, 136 (1905); Maracineanu, *Comptes Rendus*, 176, 1879.

‡ S. Maracineanu, *Thèse de Doctorat*, Paris (1924).

§ These investigations are quoted in Meyer and Sweidler, *Radioaktivität* (1929); P. Pascal, *Traité de chimie* (1930); and elsewhere.

considerable effect in nature. By exposing radioactive substances to the sun under certain conditions, clouds and artificial rain can be induced, and this gives a further proof, though one difficult to accept, of the effect.

Prof. J. C. McLENNAN, Mr L. G. GRIMMETT and Dr JOHN READ. Szilard and Chalmers\* recently reported that when some beryllium was given a surrounding of ethyl iodide and both were irradiated with  $\gamma$ -rays, the iodide became radioactive with a decay half-period of 30 min., but that when the ethyl iodide was irradiated without the beryllium being present it was unaffected. Szilard and Chalmers suggested that the  $\gamma$ -rays caused the ejection of neutrons from the beryllium atoms, and that the neutrons excited the radioactivity.

At the Radium Institute the experiment of Szilard and Chalmers was repeated by us, but iodine was used in place of ethyl iodide. It, too, became radioactive, and gave 314 Geiger-Müller kicks diminishing to 12 per min. When the iodine without the beryllium was irradiated, it again became radioactive, but to a much less degree, 45 kicks diminishing to 10 per min. being recorded. In both cases the half-period was 30 min. When the beryllium was surrounded by a silver cylinder and irradiated with  $\gamma$ -rays, the silver became radioactive, giving 50 kicks diminishing to 12 per min. with a half-period of two minutes. When the silver alone was irradiated it was unaffected. These half-periods, it will be recalled, were the same as those obtained by Fermi, who used radon plus beryllium as a neutron source. We consider that these results confirm Szilard and Chalmers's conclusion that beryllium ejects neutrons when irradiated with  $\gamma$ -rays.

Experiments are in progress to determine why the iodine becomes radioactive when no beryllium is present.

Dr L. SZILARD. The Fermi effect can be used as an indicator for the detection of neutron radiations. It may prove to be of special value for the investigation of neutron radiations in the presence of a strong  $\gamma$ -radiation. One might expect that even slow neutrons will induce radioactivity in elements which, like iodine, transmute in the Fermi effect into their own radioactive isotope, but further experiments are necessary to settle this point. Meanwhile T. A. Chalmers, of St Bartholomew's Hospital, and I have worked out a method of isotopic separation which makes it possible to concentrate chemically the activity in the case of iodine and other elements which show a Fermi effect of this type. We used this method of isotopic separation to search for new neutron sources. By irradiating 25 gm. of beryllium with the penetrating radiation from 150 mgm. radium and exposing 100 c.c. ethyl iodide to the radiation excited in the beryllium we could induce radioactivity in iodine, and separate chemically the radio-iodine from the ethyl iodide in the form of a silver iodide precipitate. This precipitate showed a strong activity, decaying with a period of 30 min., the initial activity being more than 15 times stronger in the presence of beryllium than in its absence. About half of the residual activity in the control experiment may be due to neutrons coming directly from the radium source,

\* *Nature*, 134, 494 (1934).

the other half represents the natural background effect of the counter. Apparently the  $\gamma$ -rays of radium liberate neutrons from beryllium, which induce a strong Fermi effect in iodine. The 30 min. and the six hours half-periods of bromine can also be strongly excited by these neutrons, as we have shown in co-operation with E. Glückauf. I was very much interested to hear just now that Prof. McLennan has repeated some of our experiments and was able to confirm our results. If we determine which elements show a Fermi effect when exposed to neutrons from a  $\gamma$ -ray disintegration we get by means of very simple experiments some information both regarding the processes involved in the Fermi effect and in the  $\gamma$ -ray disintegration. By using the Fermi effect one could thus supplement in some respects the method of Chadwick and Goldhaber, who were the first to detect a  $\gamma$ -ray disintegration in their pioneer work on heavy hydrogen. I wish to take this opportunity to mention that this work has been carried out in the Physics Department of St Bartholomew's Hospital and was made possible by the very kind co-operation of Prof. Hopwood.





DISINTEGRATION AND SYNTHESIS OF  
NUCLEI AND ELEMENTARY  
PARTICLES



# PHOTOELECTRIC DISINTEGRATION OF THE DIPLON

BY H. A. BETHE AND R. PEIERLS

Manchester

**ABSTRACT.** The problem of the photoelectric disintegration of the diplon is discussed theoretically, as also the excitation of diplons by electrons and by photons, and the scattering of neutrons by protons. The latter process should give an experimental method of distinguishing whether the forces between a neutron and a proton are exchange forces or ordinary ones, but it is concluded that the necessary experimental conditions could not at present be attained.

CHADWICK has shown recently that a diplon may be split into a neutron and a proton by hard  $\gamma$ -rays. The probability of this process can be calculated from quantum-mechanics and corresponds to a cross-section of the order of  $10^{-27}$  cm.<sup>2</sup>, which increases with increasing frequency of the  $\gamma$ -ray, reaches a maximum for  $h\nu =$  twice the ionization-potential, and then decreases again.

The calculation of the cross-section is independent of an exact knowledge of the forces between the neutron and the proton, whether ordinary forces or exchange forces (models of Wigner, Majorana and Heisenberg\*). The probability is also practically independent of the special law of force between the two particles. This is due to the fact that the forces act only over a very short range, which is small compared with the radius of the diplon, as may be proved from the mass defects of heavy hydrogen and of helium. It has the result of making the wave function a simple exponential over the larger part of space, viz. everywhere outside the region of appreciable potential energy. Therefore the wave function is almost everywhere defined without knowledge of the potential, and the optical transition probability may be calculated with great certainty.

Diplons could also be excited by fast electrons, the cross-section being about one hundred times smaller than for excitation by light. The scattering of light by a diplon always turns out to be smaller than for a free proton, the corresponding cross-section being of the order of  $10^{-32}$  cm.<sup>2</sup>; the scattering of light by nuclei seems therefore to be unobservably small. The emission of radiation in the recombination of proton and neutron can be calculated from thermodynamical considerations. It is smaller by a factor of the order of 1000 than the photoelectric absorption. The experiments of Lea† therefore cannot be explained by this recombination radiation.

\* E. Wigner, *Phys. Rev.* **43**, 252 (1933); E. Majorana, *Z. f. Phys.* **82**, 137 (1933); W. Heisenberg, *ibid.* **77**, 1 (1932); **78**, 156 (1933); **80**, 587 (1933).

† D. E. Lea, *Nature*, **133**, 24 (1934).

Connected with the problem of the dipion is the scattering of neutrons by protons. Wick\* has pointed out that from the angular distribution of the scattered neutrons, the nature of the forces between neutron and proton could be deduced, i.e. whether they are exchange or ordinary forces. For exchange forces the maximum scattering should be in the backward direction, for ordinary potentials in the forward direction. Unfortunately it will be very difficult to carry out such experiments: whereas Wick's argument holds for high energies, the opposite holds for small energies, and the scattering becomes exactly isotropic at an intermediate energy of about twenty million volts; for lower energies the asymmetry is extremely small (of the order of 1 per cent). It seems at present improbable that we shall ever obtain neutrons of energy much higher than twenty million volts, with which to observe a measurable anisotropy.

\* G. C. Wick, *Z. f. Phys.* **84**, 799 (1933); cf. also E. Wigner, *ibid.* **83**, 253 (1933).

# NUCLEAR TRANSFORMATIONS PRODUCED BY $\alpha$ -PARTICLES AND NEUTRONS

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*ABSTRACT.* The nature of the curve connecting the potential energy of an  $\alpha$ -particle with its distance from the centre of a nucleus is discussed, and the concept of the potential barrier is introduced.

The different processes which might possibly occur when an  $\alpha$ -particle penetrates into a nucleus are then classified, examples being given where any are known.

The only class considered in detail is that where an  $\alpha$ -particle is captured, and a proton or neutron ejected. In general, the emitted protons fall into distinct groups, each with a definite energy. It appears that when a proton of less than the maximum energy is emitted, the final nucleus is left in one of several possible states of excitation.

Evidence as to the existence and location of resonance levels in the bombarded nuclei is obtainable by using  $\alpha$ -particles of varying residual range; it is found that the proton yield passes through a series of maxima corresponding to these levels.

A table is given showing the heights of the potential barriers, and the resonance levels for a number of isotopes of the lighter elements.

The potential energy curve for a neutron in the field of a nucleus is of quite a different form, there being now no potential barrier preventing free entry of the particle. Consequently heavy as well as light elements can be successfully attacked by neutron bombardment.

The disintegration of nitrogen by neutrons is discussed in detail; there is no doubt that in many cases the neutron is captured and an  $\alpha$ -particle expelled, leaving an atom of boron as residue, but there are definite indications that some other process may also occur.

The same is true of the disintegration of carbon, oxygen, fluorine or neon by neutrons; capture of the neutron and emission of an  $\alpha$ -particle is the most probable mode.

Among the heavier elements, several types of reaction seem to occur: after capture of the neutron, there may be emission of a proton or an  $\alpha$ -particle, but in some cases it does not appear that any other particle is emitted. Quite frequently the residual nucleus is radioactive and breaks up with the ejection of a  $\beta$ -particle. The interaction between a neutron and a heavy nucleus can also take another form, the bombarded particle merely being raised to a higher quantum state without capturing the neutron. The energy of excitation is subsequently emitted as a quantum of  $\gamma$ -radiation.

## § 1. TRANSFORMATIONS PRODUCED BY $\alpha$ -PARTICLES

WHEN  $\alpha$ -particles pass through matter some of them may make a close collision with atomic nuclei. If the energy of the incident  $\alpha$ -particles is high enough, the particles will be able occasionally to penetrate the potential barrier and reach the inside of the nucleus. Different processes may then take place. The  $\alpha$ -particle may escape from the nucleus without losing energy, in which case it will reappear as an elastically scattered  $\alpha$ -particle; such a process as this is responsible for the devia-

tions, generally called "anomalous scattering," from the Rutherford scattering laws based on a Coulomb field of force. Or the  $\alpha$ -particle may give up some, or all, of its energy to the nucleus, thereby causing changes in the state of the bombarded nucleus.

Before describing the various possible nuclear changes in detail we shall first consider briefly the entry of the  $\alpha$ -particle into the nuclear system.

It is now generally assumed that the potential energy of an  $\alpha$ -particle in the electric field of a nucleus may be represented approximately by a curve such as that shown in figure 1. The potential energy varies as  $1/r$ , corresponding to a Coulomb field of force, at distances greater than a certain distance  $r_0$ . Within this distance the

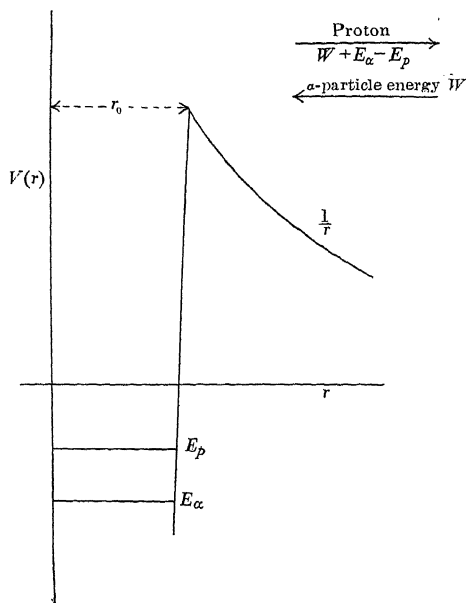


Figure 1.

force between the  $\alpha$ -particle and the nucleus is attractive and the potential falls rapidly. We may say that the region of attractive force is the "inside" of the nucleus and call  $r_0$  the "nuclear radius." If an  $\alpha$ -particle of mass  $M$ , charge  $ze$ , and velocity  $V$  passes through matter of atomic number  $Z$ , then the closest distance to which it can approach a nucleus is  $4Ze^2/MV^2$ . If this distance is greater than  $r_0$  the particles will not in general be able to reach the region of attractive forces, that is, to get inside the nucleus. Consequently the scattering of the particles will be normal and there will be no nuclear transformations. We may thus expect to find that the chance of producing nuclear transformations increases with the energy of the incident  $\alpha$ -particles and decreases with increasing atomic number of the nucleus. This is in general the case. Moreover, with the most energetic  $\alpha$ -particles at our disposal,

those of thorium C' of energy nearly 9 million e.V., no nuclear disintegrations have been found with elements of higher atomic number than potassium. This suggests that the height of the potential barrier of potassium against the entry of  $\alpha$ -particles must be at least 9 million volts and that  $r_0$  is not more than  $6 \times 10^{-13}$  cm. Observations of anomalous scattering and of disintegration lead in some instances to fairly definite values for the height of the barrier, and, on the above rather simplified picture, to values of the critical distance  $r_0$ . The results show that the height of the nuclear barrier increases with the atomic number  $Z$ , but rather more slowly; correspondingly, the critical distance  $r_0$  increases very slowly with the atomic number.

We return now to the consideration of the different nuclear changes which may occur when an  $\alpha$ -particle penetrates into the nucleus. These may be classified as follows:

Class 1. The  $\alpha$ -particle may give up part of its energy in exciting the nucleus to a higher state. The  $\alpha$ -particle escapes, and the nucleus will return to its former (ground).state with the emission of energy as a quantum of radiation\*.

*Example.* When lithium is bombarded by  $\alpha$ -particles of low energy, a  $\gamma$ -radiation of  $h\nu = \text{ca. } 6 \times 10^5$  e.V. is emitted†. It seems that the only reasonable explanation of all the evidence is to assume that this radiation is due to an inelastic collision of an  $\alpha$ -particle resulting in an excitation of the  $\text{Li}^7$  nucleus.

Although this is the only certain example of this process, there is some evidence that it occurs in other cases‡, e.g.  $\text{N}^{14}$ ,  $\text{F}^{19}$ , and possibly  $\text{Al}^{27}$ , and it may indeed be fairly frequent.

Class 2. The  $\alpha$ -particle gives up some of its energy in ejecting a particle from the nucleus, the  $\alpha$ -particle escaping capture. This type of transformation is akin to Class 1, for it corresponds to a process of excitation in which the excited particle is raised to a level of positive energy from which it can escape through the potential barrier, instead of falling back to the ground state with the emission of radiation.

So far no example of this type of transmutation is known, except possibly the disintegration of the diplon



Some evidence that this process takes place when heavy hydrogen is bombarded by fast  $\alpha$ -particles has been obtained by Dunning§.

Class 3. The  $\alpha$ -particle may be captured by the nucleus and a nucleus, higher in atomic number by 2, may be formed. The surplus energy can be emitted as a quantum of radiation. This process is theoretically very unlikely and so far no example is known.

Class 4. The  $\alpha$ -particle may be captured by the nucleus and another particle ejected. This is the usual type of transmutation produced by  $\alpha$ -particles.

\* The  $\alpha$ -particle may itself be excited in a collision. This is very unlikely for we should expect a large amount of energy to be required to raise an  $\alpha$ -particle to an excited state.

† Bothe and Becker, *Z. f. Phys.* **66**, 289 (1930); Webster, *Proc. R.S. A*, **136**, 428 (1932).

‡ Savel, *Comptes Rendus*, **198**, 1404 (1934).

§ Dunning, *Phys. Rev.* **45**, 586 (1934).



The particle emitted from the nucleus may be a proton or a neutron\*. In many cases either a proton or a neutron may be emitted. Thus aluminium bombarded by  $\alpha$ -particles emits both protons and neutrons. The processes which take place are assumed to be

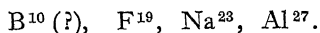


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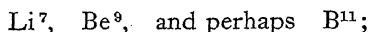


[The nucleus  $\text{P}_{15}^{30}$  is unstable and later changes into  $\text{Si}_{14}^{30}$  by the emission of a positive electron. Such transformations as this are described in the article on "Artificially Produced Radio-elements" by Mons. and Mme Joliot.]

The following nuclei give both protons and neutrons:



Other nuclei give a neutron emission only:



while so far only a proton emission has been observed from  $\text{N}^{14}$ .

Direct evidence of the capture of the  $\alpha$ -particle has been obtained in one case only, that of nitrogen, from observation with the expansion chamber†; there can be little doubt, however, from the nature of the energy changes, that it is a general feature of these transmutations.

### *Disintegration with emission of protons*

The cases of disintegration in which a proton is emitted have been investigated in much greater detail than the others, and we shall therefore consider them more closely.

It is convenient to describe the nature of the experimental results and their interpretation by the use of a particular example, and we shall take the case of aluminium.

We assume that the  $\alpha$ -particles and the proton in a nucleus are in definite energy levels. The captured  $\alpha$ -particle of kinetic energy  $W$  will fall into a level  $-E_\alpha$ , say (figure 1) and a proton will be emitted from a level  $-E_p$ . Then the kinetic energy of the ejected proton will be approximately  $W + E_\alpha - E_p$ , neglecting the energy of the residual nucleus. Thus, in this simple picture, a homogeneous beam of  $\alpha$ -particles incident on a very thin foil of aluminium should give rise to the emission of protons of the same energy (in the same direction). Figure 2*a* shows the results of such an experiment‡, using  $\alpha$ -particles of velocity  $1.60 \times 10^9$  cm./sec. The ordinates represent the number of protons which traverse thicknesses of mica given as equivalent centimetres of air by the abscissae. It is seen that the protons consist of two definite groups. Later observations§, in which  $\alpha$ -particles of velocity

\* Possibly in some cases a dipion,  $\text{H}^2$ , may be ejected, as Perrin has suggested may occur with nitrogen.

† Blackett, *Proc. R.S. A*, 107, 349 (1925).

‡ Chadwick and Constable, *Proc. R.S. A*, 135, 48 (1932).

§ Duncanson and Miller, *Proc. R.S. A*, 146, 396 (1934); see also Haxel, *Z. f. Phys.* 88, 346 (1934).

$1.92 \times 10^9$  cm./sec. were used, have shown that there are at least four groups of protons. These results are represented in a simplified form by the diagram of figure 2*b*. The groups of figure 2*a* correspond to the two groups of longer range of figure 2*b*.

The occurrence of several groups of protons, rather than of a single group, can be explained by supposing that in some cases the  $\alpha$ -particle is captured into an intermediate level and a proton is emitted with the formation of an excited nucleus ( $\text{Si}^{30}$ ), which passes into the ground state with the emission of a quantum of radiation. Thus, referring to figure 5, we may suppose that the disintegration proton comes from the level indicated, which is fixed arbitrarily. Then the group (1) of protons of longest range will arise when the incident  $\alpha$ -particle is captured into the

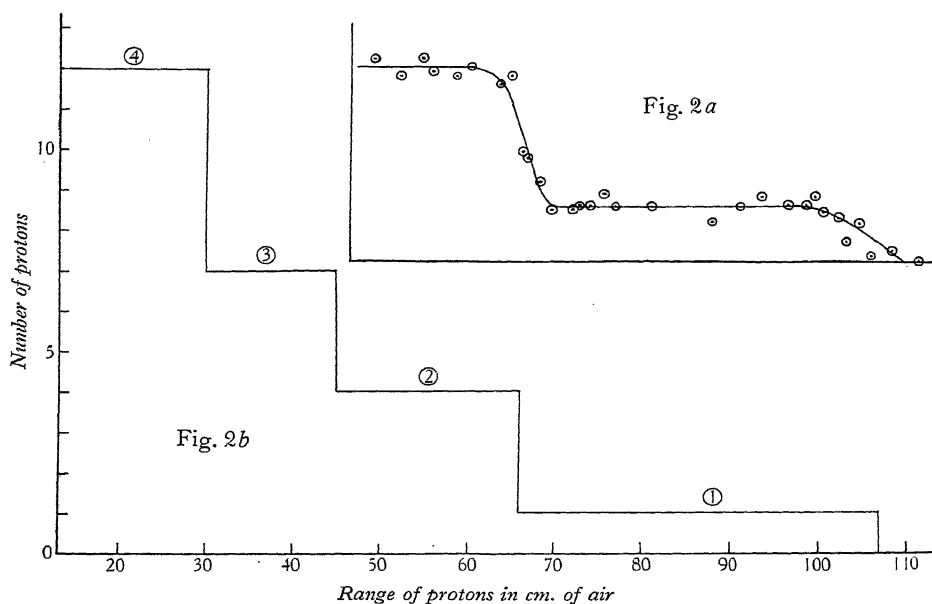


Figure 2.

level (1). Since this proton group is weak this process occurs relatively seldom. The second group of protons is emitted when the  $\alpha$ -particle is captured into level (2). The nucleus formed in this process will be in an excited state, having a surplus energy represented by the difference between the levels (1) and (2). This energy must be radiated subsequently. Similarly, the occurrence of the proton groups (3) and (4) can be explained by assuming further levels (3) and (4). Thus in the disintegration of aluminium the residual nucleus of  $\text{Si}^{30}$  may be formed in the ground state or in any one of three excited states, and the formation of an excited nucleus is much more probable. The disintegration must therefore be accompanied by the emission of  $\gamma$ -radiations corresponding to the return of the excited nuclei to the ground state. Experiment shows that some  $\gamma$ -radiation is indeed present, but the

observations are not precise enough to give any close correlation between the energy of the quanta and the energy differences between the levels (1), (2), (3) and (4).

The next point of interest concerns the entry of the  $\alpha$ -particle into the nuclear system.

When a thick foil of aluminium was bombarded by polonium  $\alpha$ -particles, of velocity  $1.60 \times 10^9$  cm./sec., the results shown in figure 3 were obtained\*. The protons emitted can be divided into eight groups which are associated in pairs (cf. figure 2*a*). The two slower groups of figure 2*b* lie outside the region of these experiments. Their ranges would be less than the minimum of figure 3. Under these conditions of experiment, collisions are taking place between aluminium nuclei and  $\alpha$ -particles of all velocities from zero up to the initial velocity of the polonium  $\alpha$ -particles; yet the disintegrations appear to be due only to  $\alpha$ -particles of certain specified velocities. The possibility of such an effect was first pointed out by

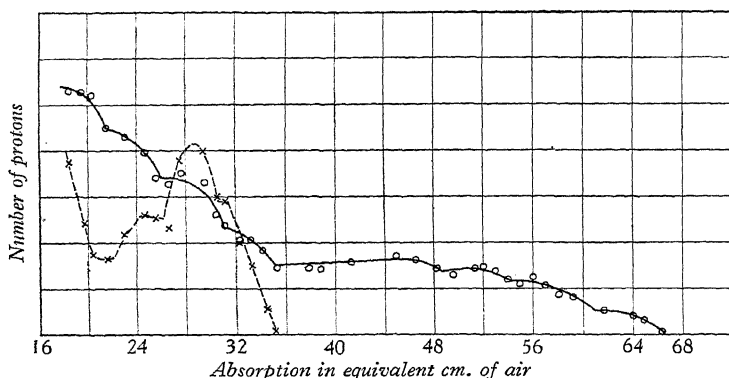


Figure 3.

Gurney†, who suggested that there may be a resonance between the incident  $\alpha$ -particle and the atomic nucleus. If the  $\alpha$ -particle has exactly the energy corresponding to a resonance level of the nucleus, its chance of penetrating the potential barrier will be much greater than if its energy were rather more or less than this. The first evidence for this resonance effect was found by Pose‡ in his experiments on the disintegration of aluminium. The observations represented by figure 3 show that there are four resonance levels of the aluminium nucleus between 4 and  $5.3 \times 10^6$  e.V. If these resonance levels did not exist, then the  $\alpha$ -particles of polonium, which have a maximum energy of  $5.3 \times 10^6$  e.V., would have a very small chance of penetrating the barrier and so would cause no appreciable amount of disintegration, for the height of the potential barrier of aluminium is probably about  $8 \times 10^6$  e.V.

These four resonance levels are not sharp and they are also close together, so that it was difficult to show that  $\alpha$ -particles of energy slightly different from that of a level had a much smaller disintegration effect, corresponding to a smaller chance

\* Chadwick and Constable, *loc. cit.*

† Pose, *Z. f. Phys.* **64**, 1 (1930).

‡ Gurney, *Nature*, **123**, 565 (1929).

of penetrating the potential barrier. This has been shown more clearly by experiments\* in which a thin aluminium foil was bombarded by  $\alpha$ -particles from radium C'. The yield of disintegration protons was observed as the energy of the  $\alpha$ -particles was gradually diminished, with the results shown by the full curve in figure 4. It is seen that as the energy of the  $\alpha$ -particles is reduced the yield of protons, or the chance of penetrating into the nucleus, falls very rapidly and becomes quite small for  $\alpha$ -particles of about 5.6 cm. range (energy =  $6.8 \times 10^6$  e.V.). As the range is further reduced, the number of protons increases rapidly to a maximum and falls again to a low value, and this is followed by a second, broader, maximum. The first rapid fall in the proton yield is to be ascribed to the diminishing chance of penetration as the energy of the  $\alpha$ -particles falls below the top of the potential barrier. Then

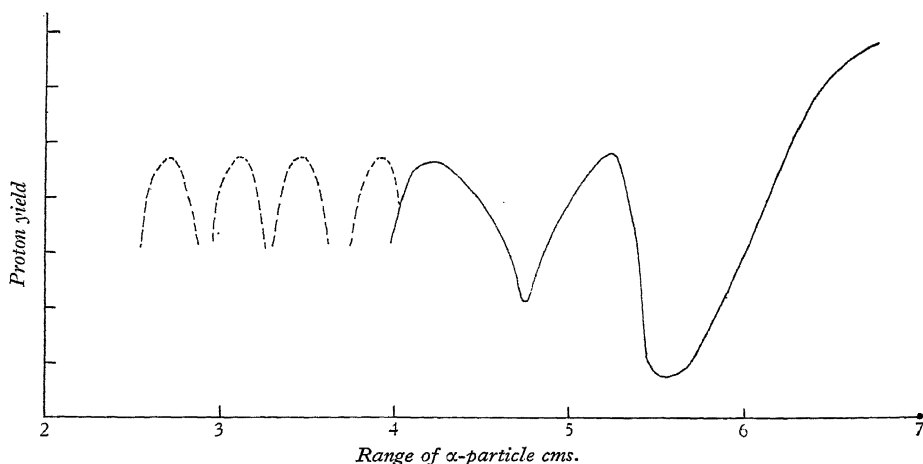


Figure 4.

as the energy of the  $\alpha$ -particle is further reduced a resonance level is reached, and the  $\alpha$ -particles again penetrate into the nucleus. The second maximum corresponds to a second resonance level. [The dotted maxima indicate the four resonance levels mentioned above but do not represent actual observations. The ordinate scale of figure 4 may be much distorted owing to experimental difficulties.]

These experiments thus give detailed information about the potential barrier of the aluminium nucleus. This information is summarized in figure 5. The top of the potential barrier has been taken to be about  $8 \times 10^6$  e.V., and a Coulomb field has been assumed for distances greater than the nuclear radius, taken to be  $4.5 \times 10^{-13}$  cm. The experiments show that  $\alpha$ -particles of energy greater than about  $6.8 \times 10^6$  e.V. can penetrate the barrier generally and they also indicate resonance levels at 6.61, 5.75, 5.25, 4.86, 4.49, and  $4.0 \times 10^6$  e.V. The widths of the resonance levels are about 200,000 to 300,000 volts. The region of the potential barrier below  $4.0 \times 10^6$  e.V. has not yet been closely investigated.

\* Duncanson and Miller, *loc. cit.*

Below ground, there are indicated the positions of the levels in which the  $\alpha$ -particle may be captured. It has been pointed out above that the kinetic energy of the proton emitted in a disintegration will depend not only upon the energy of the incident  $\alpha$ -particle but also upon the difference in energy between the level in

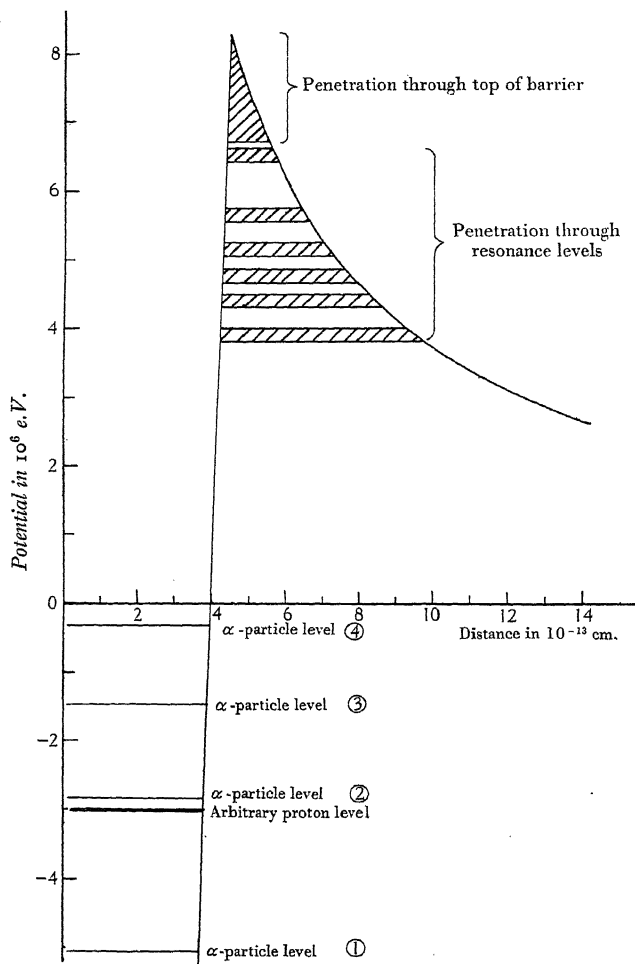


Figure 5.

which the  $\alpha$ -particle is captured and that from which the proton is emitted. The experiments give the ranges, usually measured in mica and then converted into equivalent centimetres of air, of the protons liberated by  $\alpha$ -particles of known velocity. The relation between the range in air of a proton and its velocity is now well established, and a reasonably accurate estimate of the velocity of the protons can be made from the range measurements. The change of kinetic energy in the

disintegration process can then be calculated. If  $v_p$  is the velocity of the proton of mass  $m_p$ , ejected in a direction making an angle  $\theta$  with the direction of motion of the incident  $\alpha$ -particle, of mass  $M$  and velocity  $V$ , the energy released in the disintegration will be

$$Q = \frac{1}{2m_n} [m_p v_p^2 (m_p + m_n) - MV^2 (m_n - M) - 2MVm_p v_p \cos \theta],$$

where  $m_n$  is the mass of the residual nucleus. The change of kinetic energy,  $Q$ , corresponds to the difference in energy between the level in which the  $\alpha$ -particle is captured and the level from which the proton is emitted.

The energy changes corresponding to the four groups of protons of figure 2*b* are  $+2.07$ ,  $-0.16$ ,  $-1.53$ , and  $-2.67 \times 10^6$  e.V.

We assume that the proton is always emitted from the same level, and we suppose that the  $\alpha$ -particle may be captured in any one of four levels, three lying above the proton level and the final stable level being  $2.07 \times 10^6$  volts below it. Since the experiments give the relative and not the absolute positions of the levels, an arbitrary value has been chosen for the proton level in figure 5, and the positions of the  $\alpha$ -levels are indicated relative to this.

Table 1

Element	Minimum height of barrier $10^6$ e.V.	Resonance levels $10^6$ e.V.	Number of proton groups
Be <sup>9</sup>	3.5	2.5; 1.4	2 at least (neutron)
B <sup>10</sup>	3.6	ca. 3.0	5
B <sup>11</sup>	3.7	2.4	1 (neutron)
N <sup>14</sup>	4.1	3.5	1
F <sup>19</sup>	5.0	4.0; 3.4	2 at least
Na <sup>23</sup>	—	1 at least	2 at least
Mg (?)	6.5	6.3; 5.7	2 at least
Al <sup>27</sup>	6.8	6.61; 5.75; 5.25; 4.86; 4.49; 4.0	4
P <sup>31</sup>	—	—	3 at least

The diagram of figure 5 contains in a condensed form our knowledge about the interaction of an  $\alpha$ -particle and an aluminium nucleus. Similar information can be deduced from the experiments on the transmutation of other elements. The results show the same general characteristics. Thus the experiments\* with boron†

\* Paton, *Z.f. Phys.* **90**, 586 (1934); Miller, Duncanson and May, *Proc. Camb. phil. Soc.* **30**, 549 (1934).

† Boron consists of two isotopes, B<sup>10</sup> and B<sup>11</sup>. The proton emission is here attributed entirely to B<sup>10</sup>.

show that the height of the potential barrier is about  $3.6 \times 10^6$  e.V., there is a resonance level at about  $3.0 \times 10^6$  e.V., and at least five groups of protons are liberated by a single group of  $\alpha$ -particles. The corresponding energy changes are  $+3.1$ ,  $+0.4$ ,  $-0.1$ ,  $-1.0$ , and  $-1.86 \times 10^6$  e.V. Thus the residual nucleus,  $C^{13}$ , can be formed in three excited states as well as in the ground state. The disintegration is accompanied by the emission of  $\gamma$ -rays and a rough measurement\* has given a value of about  $3 \times 10^6$  e.V. for the quantum energy. This is in fair agreement with the energy changes deduced from the proton groups.

In Table 1 we summarize the information which the transmutation experiments give about the potential barriers of nuclei. Data on  $Be^9$  and  $B^{11}$ , which give neutrons when disintegrated by  $\alpha$ -particles, are also included. The values given for the heights of the barriers are the energies of the  $\alpha$ -particles which just begin to penetrate through the top; the true heights will be slightly greater than these values.

## §2. TRANSFORMATIONS PRODUCED BY NEUTRONS

It has been pointed out in the previous section that no disintegration of any nucleus of higher atomic number than potassium has been observed under the bombardment of the fastest available  $\alpha$ -particles. This limitation of the effect of  $\alpha$ -particles is ascribed to the Coulomb forces between the  $\alpha$ -particle and nucleus; these impose a minimum distance of approach which increases with the atomic number of the nucleus and soon becomes so large that the chance of the  $\alpha$ -particle entering the nucleus is vanishingly small. In the case of the collisions of neutrons with atomic nuclei there is, however, no limitation of this kind. The force between a neutron and a nucleus is assumed to be inappreciable except at very small distances, when it increases very rapidly and is attractive. The potential energy of a neutron in the nuclear field may be roughly represented by the curve of figure 6. Thus even slow neutrons are able to penetrate into a heavy nucleus. The possibility of nuclear transformations by neutrons is then limited not so much by the conditions for entry into the nucleus as by the conditions imposed by the energy necessary for the transformations. Moreover, the energy conditions may often be more easily fulfilled in the case of neutrons than in the case of  $\alpha$ -particles, for the available energy includes mass energy as well as kinetic energy. The mass of the neutron is greater than the greatest mass difference which occurs as between two stable nuclei with consecutive mass numbers, while the mass of the  $\alpha$ -particle is less than four times this difference. Thus we may again expect the neutron to prove more effective than the  $\alpha$ -particle as a promoter of nuclear transformations. These general considerations are supported by the experiments. Without employing neutrons of very great energy (of maximum energy little higher than the maximum energy of the  $\alpha$ -particles used in corresponding experiments) it has been found possible to produce transformations in even the heaviest nuclei, and with such varied results that all types of transformation (Classes 1 to 4, p. 97) appear to be exemplified. There is some difference

\* Becker and Bothe, *Z. f. Phys.* **76**, 421 (1932).

between the transformations observed with light and with heavy elements. With light elements transformations of Class 4 are relatively frequent; the neutron is captured and an  $\alpha$ -particle or a proton (perhaps in some cases a dipton) may be emitted. As the atomic number of the bombarded element increases, this type of transformation must become rapidly rarer, for as the potential barrier around the

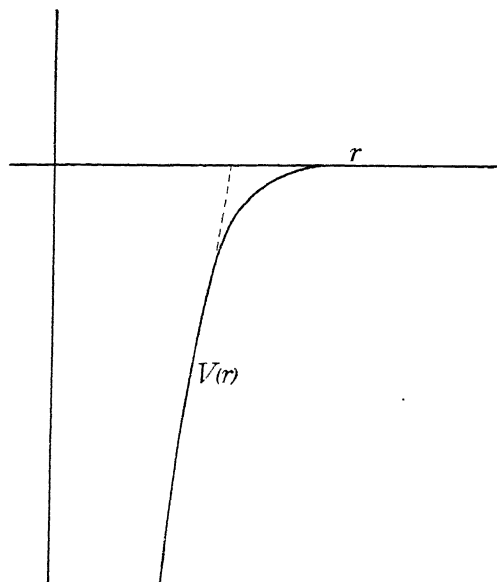


Figure 6.

nucleus increases in height, the probability of escape of a heavy, positively charged particle will become exceedingly small unless its energy is very high.

It is of interest to note that detailed information concerning these disintegrations has been obtained exclusively by use of the expansion chamber, whereas this method has been only rarely used to study the disintegrations produced by  $\alpha$ -particles. The reasons for this difference in technique are not far to seek. When disintegration is produced by  $\alpha$ -particle bombardment, the range of the particle emitted in the disintegration is usually considerably greater than the residual range of the  $\alpha$ -particle which is effective. Thus, since radioactive sources are available which emit  $\alpha$ -particles of a single velocity only, it is not difficult to observe one of the products of disintegration entirely outside the range of action of these particles and so to arrange matters that, without direct observation of any disintegration event, it is possible to be reasonably certain of the velocity of the particle responsible, within sufficiently narrow limits. There is no necessity, therefore, for the use of the expansion chamber. Three independent data, the energy of the  $\alpha$ -particle, the range (and so the energy) of the proton and the angle between the directions of motion of  $\alpha$ -particle and proton may be determined without its aid. This is sufficient to determine the energy balance in the nuclear process uniquely—always assuming, of course, that initial and final products are known and that conservation of mass-energy and momentum obtains.

When disintegration is caused by neutron bombardment, on the other hand, the ranges



of the disintegration particle and of the residual nucleus are both several orders of magnitude smaller than the range of action of the neutrons; furthermore it has not been found possible, hitherto, to employ sources which provide neutrons of a single velocity only. Developments now in progress may remedy this defect and, in addition, furnish sources of much greater intensity than any at present available, but the expansion chamber will remain indispensable for investigations under this head. The data which it provides are the ranges of the (charged) products of disintegration and the angle (or angles) between their directions of motion. If kinetic energies can be deduced from observed ranges this material is again sufficient to determine the numerical details appropriate to any capture disintegration process which may be assumed to be involved. Passage of a neutron through the expansion chamber results in no continuous cloud track such as is observed with other particles. This is at once an advantage and a limitation. There is no restriction on the strength of source which may be employed, as there is in the  $\alpha$ -particle case, but there is a lack of knowledge of the direction of incidence of the neutron responsible for any disintegration event which is observed. However, this knowledge is indispensable only when a suspected non-capture disintegration requires precise investigation. For the present, therefore, the advantage of increased strength of source more than compensates for this lack of knowledge.

### *The disintegration of nitrogen by neutrons*

The first experiments were made with the neutrons from polonium-beryllium and nitrogen in the expansion chamber. Here Feather\* observed about thirty examples of paired tracks characteristic of disintegration. Measurement and calculation showed that lengths and angles for many of these disintegration pairs could be explained on the assumption that in each case a neutron had been captured by a nitrogen nucleus and an  $\alpha$ -particle expelled. On this assumption the residual nucleus was that of the heavier isotope of boron—



Evidence for the formation of boron nuclei with different amounts of energy of excitation was afforded by the considerable spread in the values of the kinetic energy balance calculated for individual disintegration events. Subsequently, more extensive data obtained by Harkins, Gans and Newson†, in similar experiments, confirmed this result. Further material has been provided by Meitner and Philipp‡ and by Kurie§. There is a spread of energy values, but it cannot be claimed that the measurements—or the data used in their interpretation (range-velocity relations which are not sufficiently well known)—are accurate enough to establish conclusively the excitation energies of the nucleus in question. It is merely probable that there are two or three excited states within  $5 \times 10^6$  e.V. of the ground state. Now the nucleus  $\text{B}^{11}$  may be produced in another reaction, and it is interesting to observe that more direct evidence in that case points to excitation energies of the same order of magnitude. Cockcroft and Walton|| have established the production of at least three groups of protons in the disintegration



\* *Proc. R.S. A*, 136, 709 (1932).

† *Z. f. Phys.* 87, 484 (1934).

|| *Proc. R.S. A*, 144, 704 (1934).

† *Phys. Rev.* 44, 529 (1933).

§ *Bull. Amer. Phys. Soc.* 9 (3), 8 (1934).

whereby excited states of  $2.2$  and  $4.5 \times 10^6$  e.V. excess energy are indicated\*. It would appear that these states are the same as those involved when the nucleus  $B^{11}$  is produced as the result of the disintegration of nitrogen by neutrons (equation (1)). In order to complete our description of either transformation it will be necessary to investigate (cf. p. 99) the  $\gamma$ -rays which are emitted in these disintegrations. This has yet to be attempted for the neutron-produced change, but preliminary results in the other case† have already established the production of some  $\gamma$ -radiation, the precise origin of which is not yet established.

It has previously been mentioned that not all the examples of disintegration obtained in the first experiments with nitrogen could be explained in terms of equation (1). At least it proved impossible to adopt this as the sole explanation, if capture of a neutron proceeding directly from the source were to be assumed. In the results of Harkins, Gans and Newson an exactly similar difficulty appeared. One solution is to ascribe, as these authors have done, all apparently anomalous disintegrations to scattered neutrons, another is to assume some non-capture process, such as that in which a proton is emitted and  $C^{13}$  is produced,



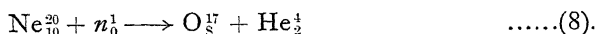
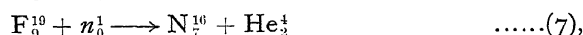
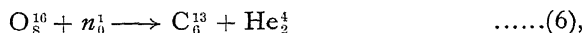
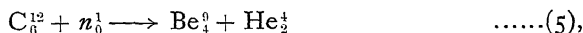
Whilst it is obvious that scattered neutrons must to some extent be responsible, it is not as yet clear whether disintegration without capture is in fact taking place. Whatever the final decision on this point may be, it appears increasingly unlikely that equation (1) can represent all the results. Kurie‡ has recently published photographs suggesting that in certain cases a proton or other singly charged nucleus must be emitted, and Feather§, in a rediscussion of the subject, has put forward evidence for the reaction



It is obvious that our knowledge is still very imperfect here.

### *The disintegration of other light elements*

In addition to nitrogen, most of the common gases have been examined in the expansion chamber, and in this way direct evidence has now been obtained for the disintegration of carbon, oxygen, fluorine and neon when bombarded by neutrons. It is very probable that in each case the chief mode of disintegration results in the emission of an  $\alpha$ -particle after capture of the neutron. Equations (5) to (8) express this fact and in addition indicate the residual nuclei which result in the particular cases:



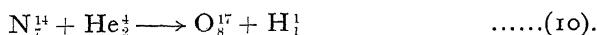
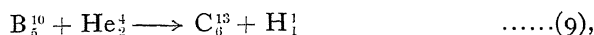
\* A possible fourth group of protons suggests a third excited state at  $6.8 \times 10^6$  e.V. energy.

† Lauritsen and Crane, *Phys. Rev.* **45**, 493 (1934). See also their report in this volume, p. 130.

‡ *Phys. Rev.* **45**, 904 (1934).

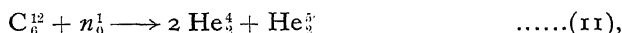
§ *Proc. R.S. A*, **142**, 689 (1933).

Except as concerns the disintegration of carbon (equation (5)), there is already sufficient evidence to show that the energy change is not constant for all examples of a single process; nuclei  $C^{13}$ ,  $N^{16}$ ,  $O^{17}$  are sometimes formed with energy content in excess of the normal. Now the nuclei  $C^{13}$ ,  $O^{17}$  may each be obtained as the result of a disintegration process in which an  $\alpha$ -particle is captured and a proton is emitted. We have:



Here there is evidence, from the nature of the proton emission, to show that the nucleus  $C^{13}$  may exist temporarily with energy of excitation of 2.7, 3.2, 4.1, or  $5.0 \times 10^6$  e.V.\*; and, of a negative character, to suggest that, for excitation of the nucleus  $O^{17}$ , energy in excess of  $1.5 \times 10^6$  e.V. is necessary†. Such evidence as there is from the neutron-produced disintegrations does not run counter to either of these results, although it cannot be claimed that in its present state it is sufficiently trustworthy or extensive to be cited in support of them.

Finally, as concerns carbon, there is very direct evidence for disintegration under neutron bombardment following an alternative mode. Chadwick, Feather and Davies‡ have obtained one pair of expansion chamber photographs showing the tracks of three heavy particles originating in a single point in space. Quantitatively their observations may be explained either on the basis of the capture disintegration



or on a basis of non-capture,



From various points of view it appears that there is a slight balance of likelihood in favour of the second of these explanations.

On Plate I are reproduced two of the previously published photographs of paired disintegration tracks in nitrogen and oxygen (numbers 1 and 2, respectively), the two views of the three-particle disintegration of carbon referred to above (numbers 3 and 4) and a hitherto unpublished photograph (number 5) showing two disintegration events in an air-filled chamber. The neutrons of polonium-beryllium were employed in all cases.

#### *Evidence for the disintegration of the heavier elements*

The disintegration of fluorine by neutrons has already been discussed. Harkins, Gans and Newson§ pointed out that, whilst the evidence from cloud photographs indicated the production of an unknown nucleus,  $N^{16}$ , there was nothing on the photographs to show whether this nucleus was the final product or whether it subsequently passed into a stable nucleus,  $O^{16}$ , by a  $\beta$ -particle change. Later, Fermi|| discovered a  $\beta$ -activity in calcium fluoride which had been irradiated with

\* See p. 104.

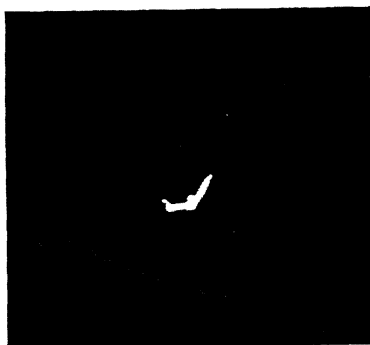
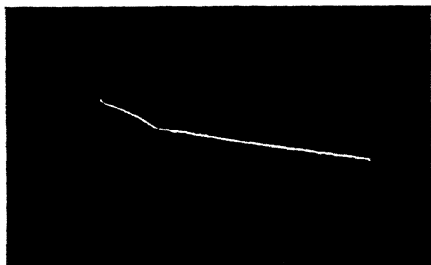
† *Proc. Camb. Phil. Soc.* 30, 357 (1934).

‡ *La Ricerca Scientifica*, 5 (1), 283 (1934).

§ Pollard, *Proc. R.S. A*, 141, 375 (1933).

§ *Phys. Rev.* 44, 945 (1933).

INTERNATIONAL CONFERENCE ON PHYSICS, VOL. I  
(CHADWICK AND FEATHER)





the neutrons from radon-beryllium. This activity, which decayed to half value in about 10 sec., he attributed to the unknown nitrogen isotope formed in the primary disintegration of fluorine by neutrons. The recent observation of Bjerger and Westcott\*, that no activity is produced when neutrons of  $2 \times 10^6$  e.V. energy are employed, lends weight to this assumption. According to the observed values of the energy balance in reaction (7), neutrons of this low energy would not be expected to be effective in the primary disintegration.

Fermi's initial observations concerned aluminium and fluorine; since then about fifty elements have been shown to give similar effects. In each case irradiation by neutrons is followed by the emission of  $\beta$ -particles. Exponential decay periods varying from a few seconds to several days have been found, whilst in certain cases the decay of activity has been shown to be complex. A considerable amount of information of this kind, and rough data concerning the energies of the  $\beta$ -particles, is rapidly accumulating, with very little direct evidence to show to what nuclei the radioactive properties are to be ascribed or what the primary reactions are which give rise to them. It is with this aspect of the phenomena that we are here concerned. Hitherto the only methods of investigation have been chemical methods; these have shown that the subsequent activity after neutron bombardment may be possessed by an element two places, or one place, removed in the periodic table from the element bombarded—or, sometimes, by an unstable isotope of that element itself. Thus, doubly charged or singly charged particles may be emitted in the primary disintegration; or the neutron may simply be captured with (presumably) the emission of excess energy in the form of  $\gamma$ -radiation. This last process appears to occur with vanadium, manganese, copper, arsenic, bromine, iodine, iridium and gold, the nuclear species concerned being  $V^{51}$ ,  $Mn^{55}$ ,  $Cu^{63}$ ,  $As^{75}$ ,  $Br^{79}$ ,  $Br^{81}$  (both isotopes are affected),  $I^{127}$  and probably  $Ir^{193}$  and  $Au^{197}$ . The process† itself, it will be noted, must be assigned to Class 3 of our original classification (p. 97). Singly charged particles (assumed to be protons) appear to be emitted from magnesium, aluminium, silicon, phosphorus, sulphur, chromium, iron and zinc, where, combining all our information, we may assign these reactions to the nuclei  $Mg^{24}$ ,  $Al^{27}$ ,  $Si^{28}$ ,  $P^{31}$ ,  $S^{32}$ ,  $Cr^{52}$ ,  $Fe^{56}$  and  $Zn^{64}$ , respectively‡. Finally, there is evidence for the emission of  $\alpha$ -particles from fluorine (already discussed), aluminium, phosphorus, chlorine and cobalt, or, in particular, from the nuclei  $F^{19}$ ,  $Al^{27}$ ,  $P^{31}$ ,  $Cl^{35}$  and  $Co^{59}$ .

Both protons and  $\alpha$ -particles are emitted from aluminium and phosphorus. In the latter case there is evidence§ to show that, whilst the threshold energy for the reaction



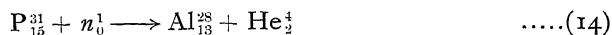
\* *Nature*, 134, 177 (1934).

† This process, as we have already pointed out in connexion with the  $\alpha$ -particle transmutations, is theoretically very unlikely. There is, however, little doubt that it does actually take place in certain cases. In other cases the evidence is not sufficient to decide the nature of the transmutation process, and it may be that the incident neutron ejects another neutron from the nucleus without itself being captured. Cf. Fermi and others, *Proc. R.S. A.*, 146, 483 (1934).

‡ In the lists given here the results of purely chemical tests are supplemented by a general survey of the data concerning decay periods—on the broad assumption that, if the same decay period occurs when neighbouring elements are activated, then a single radio-element is involved.

§ Bjerger and Westcott, *loc. cit.*

is below  $2 \times 10^6$  e.V., that effective in the alternative transformation



occurs at some higher value than this.

Nine examples have been given of nuclei which transform into unstable species by simple capture of a neutron, and five examples in which capture followed by  $\alpha$ -particle emission leads to a similar result. All these nuclei belong to elements of odd atomic number. On the other hand two, only, of the eight nuclei for which the primary disintegration involves emission of a proton, are similarly classed. Out of twenty-two cases of nuclear transformation, therefore, twenty result in unstable species for which  $Z$  is odd; in only two cases are radioactive nuclei of even atomic number produced. These results are entirely in line with well known regularities in nuclear mass and charge numbers for stable species. Elements of even atomic number frequently possess several stable isotopes, those of odd atomic number are, in general either "pure" elements or possess two isotopes whose mass numbers are two units apart. It would appear that the "missing isotopes" of odd atomic number are in most cases unstable.

The production of artificial radioactivity has provided the first reliable evidence for the disintegration of heavy elements by neutrons; it appears that quite frequently such disintegrations result in residual nuclei which are unstable. Yet there is no reason to suppose that this is invariably the case. The course of future investigations into the primary disintegrations which precede the spontaneous transformation of unstable species may well be rendered more difficult through the occurrence of other "normal" modes of disintegration.

### *Nuclear transformations of Class 1*

As the result of transformations of this class (see p. 97) the nucleus, or the incident particle, is raised to a state of higher energy, at the expense of the energy of motion of the particle, but no synthesis takes place. Subsequently a quantum of radiation is emitted from the excited system. This appears to be a very frequent mode of interaction between neutrons and atomic nuclei. The evidence, so far, is indirect;  $\gamma$ -rays have been observed, but no other conclusive proof of the occurrence of inelastic collisions has been obtained. Lea\* has investigated the production of  $\gamma$ -radiation when the elements hydrogen, carbon, aluminium, sulphur, iron, nickel, copper, zinc, silver, mercury, lead and bismuth are bombarded by the neutrons from polonium-beryllium and also, in a few cases, by the neutrons of smaller average energy from polonium-boron. In each case a positive result was recorded. The first indications of the effect were obtained with hydrogen† (differential observations were carried out with carbon and paraffin), when an estimate was made of the mean quantum energy of the radiation as  $3 \pm 1 \times 10^6$  e.V. This appears to be substantially correct. On the other hand, the interpretation originally offered, in terms of capture of the neutron and the formation of the nucleus  $H^2$ , has been variously

\* In course of publication.

† *Nature*, 133, 24 (1934).

criticized in the light of other experiments and on general theoretical grounds\*, and the position here is still uncertain. For the heavier nuclei, however, an explanation in terms of excitation without capture appears to be very probable. It is known that many of these nuclei undergo capture disintegration and it is plausible to assume that  $\gamma$ -rays are emitted as a result of such transformations, but the order of magnitude of the present effect is considerably greater than can be allowed for disintegration phenomena of the types previously studied. It is probable that as many as one-half of the close collisions between neutrons and heavy nuclei result in excitation without capture. The nuclear cross-section for this effect in iron is about  $2.2 \times 10^{-24}$  cm.<sup>2</sup>; the mean quantum energy of the radiation emitted is roughly  $1.5 \times 10^6$  e.V. Nuclear cross-sections vary in an apparently regular manner from element to element—except that the value for hydrogen is abnormally high—and less rapidly, for medium heavy and heavy elements, than the atomic number,  $Z$ . The information is too meagre to warrant detailed discussion here and further experiment is required.

\* Auger, *Comptes Rendus*, **198**, 365 (1934); Massey and Mohr, *Nature*, **133**, 211 (1934).



## TRANSMUTATIONS PRODUCED BY HIGH-SPEED PROTONS AND DIPLONS. PART I

By J. D. COCKCROFT

Cambridge

**ABSTRACT.** After a rapid review of the methods used for the production of streams of high-speed ions, a number of individual reactions are dealt with in detail.

1. Boron bombarded with protons. Here,  $\alpha$ -particles are emitted having a *continuous* distribution of energies up to a maximum of about  $5.65 \times 10^6$  e.V., together with a homogeneous group with energy  $5.8 \times 10^6$  e.V. It is assumed that the boron isotope of mass 11 captures a proton and breaks up into three  $\alpha$ -particles which will most probably recoil at angles of  $120^\circ$  to each other.

The origin of the homogeneous group is less clear, and may be due to the formation of an atom of beryllium of mass 8, or to the case where two of the  $\alpha$ -particles in the previous reaction are emitted in opposite directions, the remaining particle having then a very small momentum.

2. Boron bombarded with diplons. Here there are four groups of protons and a *continuous* distribution of  $\alpha$ -particles, the former probably due to the formation of the boron isotope of mass 11, and the latter to a reaction similar to that with protons.

Other reactions lead to the emission of neutrons, and may involve the formation of a carbon atom, though this is not certain, and yet others to the emission of positrons. In the latter case the phenomenon of artificial radioactivity is involved, the half-period of the element concerned being from 18 to 28 min. It is probable that this element is radio-carbon, the result of the positron emission being an atom of boron one unit higher than the original atom.

3. The disintegration of carbon. Under proton bombardment, carbon becomes radioactive, the decay period being 11 min. It is suggested that the first product is radio-nitrogen, the ultimate product being carbon of mass 13.

Under dipton bombardment, carbon yields protons of definite range, as well as a  $\gamma$ -radiation. The carbon also becomes radioactive, the half-life agreeing with that for carbon activated by protons. The reaction is probably the formation of radio-nitrogen (mass 13) with expulsion of a neutron, followed by the emission of a positron and another neutron, to leave an isotope of carbon one unit heavier than the original atom.

4. The disintegration of oxygen, fluorine and some heavier elements is dealt with in some detail.

The rate at which the number of disintegrations varies with the voltage applied to the bombarding particles is next discussed, in part theoretically and in part experimentally.

A table is given showing how the yield varies with voltage for seven different reactions, and the deductions to be drawn from the figures are discussed. There is also a discussion of the heights of the potential barriers round light particles, and of the chance of disintegration in certain cases after a particle has succeeded in passing the barrier.

## INTRODUCTION

THE development of methods of producing nuclear transmutation by ions speeded up in artificially produced electric fields is a recent and very rapid growth. The success of Coolidge in producing high-voltage Lenard tubes directed the attention of some, at least, of the workers in this field to the possibility of producing high-velocity ions by similar methods; and work was commenced on the subject by several laboratories about the same time in 1928. In Germany, Brasche and Lange attempted to apply high voltages from lightning to discharge tubes and later used impulse generators for the work; in California, Lawrence and his co-workers began the development of the acceleration by multiple impulses in a magnetic field which has since achieved such a remarkable success; in Cambridge the technique which had been developed by Allibone for the production of high-speed electrons was modified by Cockcroft and Walton to produce high-voltage steady potentials and to develop high-vacuum tubes suitable for the acceleration of positive ions. The stimulus for the latter work came largely from the theory which had been published about this time by Gamow and by Condon and Gurney for the penetration of charged particles through potential barriers. Whereas formerly it had been considered that potentials of several million volts would be required to make success by artificially accelerated particles feasible, the new wave mechanics showed that a proton having an energy of only a few hundred thousand volts might be expected to have an appreciable chance of penetrating the repulsive fields round the nucleus. At this time, however, it was not at all clear that transmutations leading to the emission of  $\alpha$ -particles would result. At first a search was made for the emission of  $\gamma$ -rays, which it was thought might be emitted after the penetration of the nucleus. These experiments leading to negative results, the emission of heavy particles was looked for by the most primitive of all methods, the scintillation screen, and at once bright scintillations were observed when lithium was bombarded by 100,000 volt protons. The subsequent experiments showed conclusively that the lithium nucleus captured a proton and split up into two  $\alpha$ -particles. Since that time, the transmutation of carbon, fluorine and boron has been produced by protons, and a remarkable extension of the work has come from the use of the heavy hydrogen ion, the "deuteron" or "diplon" as a bombarding particle. In their pioneer work with these ions, Lawrence, Livingston and Lewis were able to show that a quite different series of reactions took place when lithium, nitrogen and other substances were bombarded, and in particular they discovered the emission of protons which now seems to be connected with the transmutation of one isotope of a substance into the next heavier. In general, subsequent work has shown that the higher the atomic number of an element, the greater is the voltage required for its disintegration. In Cambridge, two types of apparatus have been developed; the apparatus of Rutherford and Oliphant generates intense streams of protons and diplons at energies up to 350 kV. and has been employed to investigate in great detail the disintegration of heavy hydrogen, lithium, boron and beryllium. The apparatus of Cockcroft

and Walton on the other hand generates less intense streams of ions at double the voltage and has, up to the present, proved adequate for the study of boron, carbon, nitrogen and oxygen. It seems certain, however, that in the future ions of very much higher energy will be required if a complete study of nuclear transmutations is desired. For this purpose the apparatus of Lawrence stands at present pre-eminent; the future, however, may well show the development of a wide variety of apparatus designed for this purpose.

## 1. 1. THE DISINTEGRATION OF BORON BY PROTONS

Experiments on the bombardment of boron by protons\* have shown that at voltages between 200 and 400 kV.,  $\alpha$ -particles are emitted in even greater numbers than from lithium, and that the energy distribution of the emitted particles is of quite different type from that obtained in most nuclear reactions in which homogeneous groups of particles are found. In the case of boron the  $\alpha$ -particles have a continuous distribution of energies between zero and  $5.65 \pm 0.15$  million volts, the most probable energy being about 3.6 m.V. In addition there is now clear evidence of the existence of a homogeneous group of particles having a range of 4.4 cm. and an energy of 5.8 m.V. These conclusions result from Rutherford and Oliphant's absorption curve of the particles given in figure 1 and from the data obtained by Kirchner† from Wilson chamber measurements. Curve 1 shows the original absorption curve obtained by Rutherford and Oliphant. This curve when corrected for straggling and differentiated shows that the maximum number of particles have a range of  $2.2 \pm 0.2$  cm. Curve 2 gives the result of more recent measurements on the tail of the curve which have confirmed Kirchner's report of a homogeneous group. Curve 3 gives Kirchner's figures for the number of tracks of a given range. The Wilson chamber and absorption experiments are thus now in good agreement.

The continuous energy distribution is explained by the natural assumption that the boron isotope of mass 11 captures a proton and breaks up into three  $\alpha$ -particles, since any distribution of the surplus energy of transmutation is possible between the three particles provided that momentum is conserved.

It is reasonable to assume that the most probable distribution is that in which the momentum vectors are equal and inclined at 120 degrees to each other. We then deduce that the kinetic energy appearing in the  $\alpha$ -particles will be three times the most probable energy, or  $10.95 \pm 0.75$  m.V., a figure which has to be compared with the energy expected from mass calculations, viz. 11.6 m.V. ( $B^{11} = 11.0110$ ).

It might be expected that a more accurate experimental value for the energy release might be obtained from the maximum of the energy spectrum, since this point can be obtained with more precision than the point of maximum slope of the absorption curve. From momentum considerations alone, a particle would be expected to have the maximum energy when it was emitted in a direction opposite

\* Cockcroft and Walton, *Nature*, **131**, 23 (1933); Oliphant and Rutherford, *Proc. R.S.* **141**, 266 (1933).

† *Phys. Z.* **35**, 293 (1934).

to that of two others, and in this case it would take two-thirds of the total energy. We should then obtain a total energy release of 8.5 m.V. from Oliphant and Rutherford's value for the end point. In criticism of this view, it has been argued\* that this particular distribution could not occur since two particles could not escape with zero relative velocity owing to their mutual repulsion. This classical

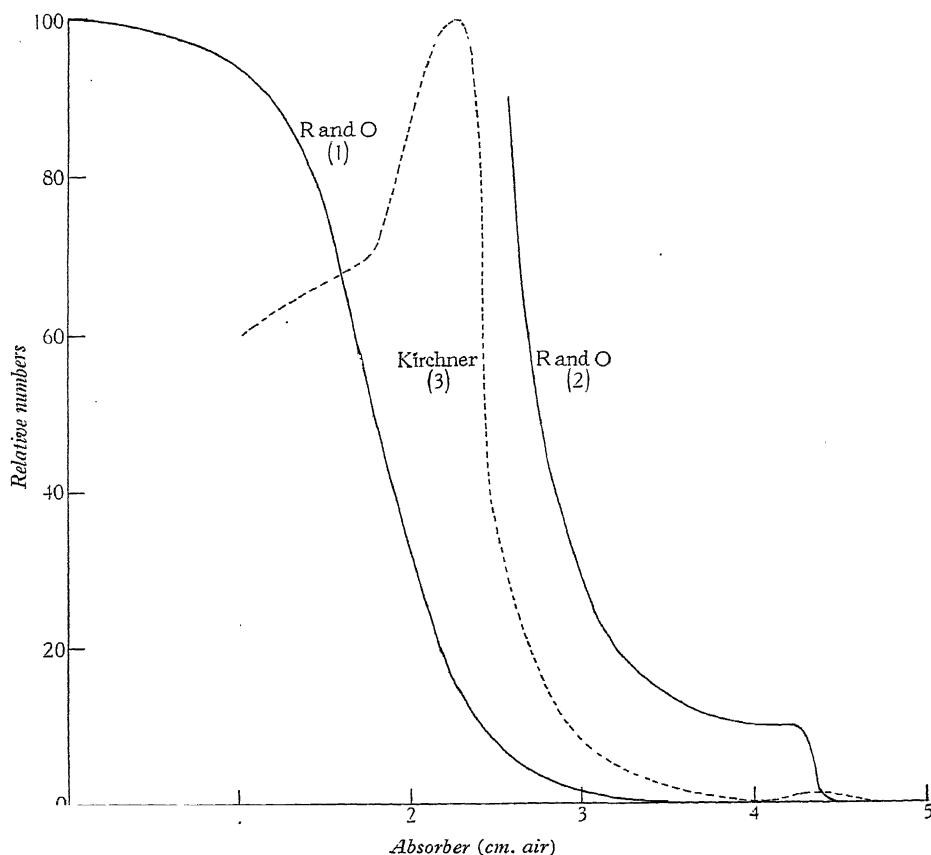


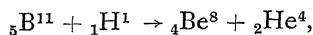
Figure 1.

argument cannot hold strictly, since by wave mechanics there is a finite chance of a particle penetrating the potential barrier of the parent nucleus even when its energy is much less than the height of the barrier, so that two particles on escape will not necessarily have kinetic energy corresponding to the height of the potential barrier. Nevertheless the chance of escape with low relative velocity will be small, so that the end point of the continuous distribution may well correspond to a distribution of

\* Lauritsen and Crane, *Phys. Rev.* March 13, 1934; Kirchner, *Naturwiss.* 25, 8, 473 (1933).

momenta similar to figure 2 (c). The minimum angle  $\theta$  would have to be of the order of 45 degrees to explain the observed end point.

The interpretation of the homogeneous group is at present uncertain. Kirchner\* ascribes this group to the reaction



and thus calculates the mass of  $\text{Be}^8$  as  $8.0074 \pm 0.0015$ , assuming Aston's value for  $\text{B}^{11}$  and that no  $\gamma$ -radiation is emitted from the  $\text{Be}^8$  nucleus. This high mass introduces difficulties about the stability of  $\text{Be}^8$ , and Rutherford and Oliphant have made the alternative suggestion that the homogeneous group results from two  $\alpha$ -particles being ejected in opposite directions (figure 2 (d)), the third particle

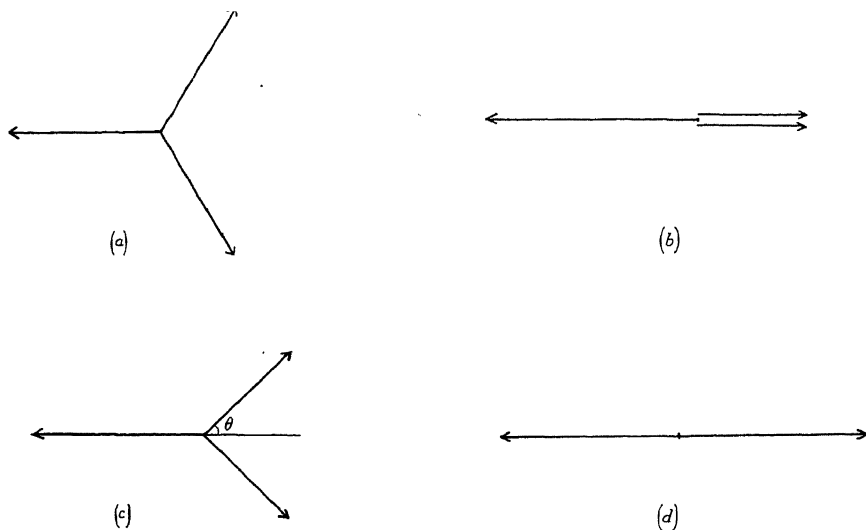


Figure 2.

having only small momentum, this particular symmetrical distribution being favoured so that an apparently homogeneous group results. The support for this hypothesis comes from the fact that the kinetic energy of two such  $\alpha$ -particles would be 11.6 m.V., a figure almost exactly in agreement with the expected energy release. It finds some additional numerical support from the data on the disintegration of boron by diplons to be given later.

Wilson chamber photographs of the disintegration of boron by protons have been obtained by Kirchner and one photograph, reproduced in figure 3, shows three radiant tracks making angles of 120 degrees with each other. Dee and Walton†, on the other hand, report several cases of three uniplanar tracks passing through a point, but state that momentum requirements were never accurately fulfilled, although this might well be due to deflexions in the tracks occurring near

the end of their range. The photograph due to Dee and Walton reproduced in figure 4 shows two tracks proceeding in opposite directions, both having a range of more than 3.5 cm. If these tracks belong to a single disintegration they ought on the hypothesis of Rutherford and Oliphant to have ranges of 4.4 cm.; unfortunately



Figure 3.



Figure 4.

no photographs exist at the moment from which ranges of the particles arising from such a disintegration can be measured with certainty. Although therefore the general nature of the boron disintegration is fairly clear, the finer details of the distribution of the three particles are still very uncertain and more Wilson chamber photographs are required to clear up the interpretation.

## I. 2. THE DISINTEGRATION OF BORON BY DIPLONS

(1) *Disintegrations leading to the emission of protons and  $\alpha$ -particles*

The disintegration of boron by diplons is a considerably more complex process than the disintegration by protons, no less than five types of radiation being emitted, whilst at least four different nuclear reactions appear to be possible.

If absorption measurements are made on the heavy particles emitted when a target of  $B_2O_3$  is bombarded by diplons\* of 500 kV. energy, the curve of figure 5 is obtained. This curve when combined with measurements of the relative ionizations produced by the particles suggested that the following heavy particles were emitted:

(1) A continuous distribution of  $\alpha$ -particles having ranges up to a maximum of  $14.3 \pm 1$  cm.†

(2) A proton group of range  $31 \pm 2$  cm., corresponding to an energy of 4.7 m.V.

(3) A proton group of range  $58 \pm 2$  cm., corresponding to an energy of 6.8 m.V.

(4) A proton group of range  $92 \pm 2$  cm., corresponding to an energy of 8.9 m.V.

(5) A proton group of range  $9 \pm 2$  cm., corresponding to an energy of 2.3 m.V.

There are also indications of a maximum in the  $\alpha$ -particle distribution at an absorber of about 9 cm., and some indication of a group having a range of about 15 cm. A complete interpretation of the absorption curve is, however, made difficult by the presence of protons.

It appears probable that the  $\alpha$ -particle disintegration is of a similar type to that produced by protons, the boron isotope of mass 10 splitting up into three  $\alpha$ -particles after the capture of the diplon. A first test of this hypothesis would be provided by a measurement of the most probable  $\alpha$ -particle energy, which on the arguments advanced for the proton disintegration should be one-third of the total expected energy release of  $19.4 \pm 0.6$  m.V., corresponding to a range of 5.2 cm. Up to the present, however, the measurements have not been made with smaller absorbers than 5 cm., since the presence of protons in the beams used in the original experiments produced large numbers of disintegrations with ranges up to 4.4 cm.

A second test is provided by the maximum energy of the  $\alpha$ -particles, which in this case should correspond to the distribution of figure 2 (c), the angle  $\theta$  being however much smaller than for protons. If, for example, we take the minimum observable relative energy of the two particles B and C to be 2 m.V., the angle  $\theta$  would be only 22 degrees and the total energy about 1.58 times the maximum  $\alpha$ -particle energy of  $12 \pm 0.5$  m.V. The total energy release would thus be  $19 \pm 0.8$  m.V. in good accord with the value expected.

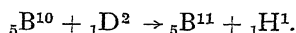
It is also interesting to note that the maximum in the  $\alpha$ -particle distribution at 9 cm. corresponds to an energy of 9 m.V. or roughly half the total energy release.

\* Cockcroft and Walton, *Proc. R.S.* 144, 704 (1934).

† The ranges given in the published work have been reduced since measurements made by Oliphant on the stopping power of mica relative to air for ranges up to 13 cm. show that an appreciable correction is required. No evidence is yet available as to the variation for protons.

Again, however, Wilson chamber experiments are required before more definite conclusions can be reached.

The disintegration with the emission of protons most probably results from the transmutation of  $B^{10}$  into  $B^{11}$ :



The expected energy release from Aston's values for  $B^{10}$  and  $B^{11}$  is 7.7 m.V. If the proton group of 92 cm. range corresponds to the maximum energy release we

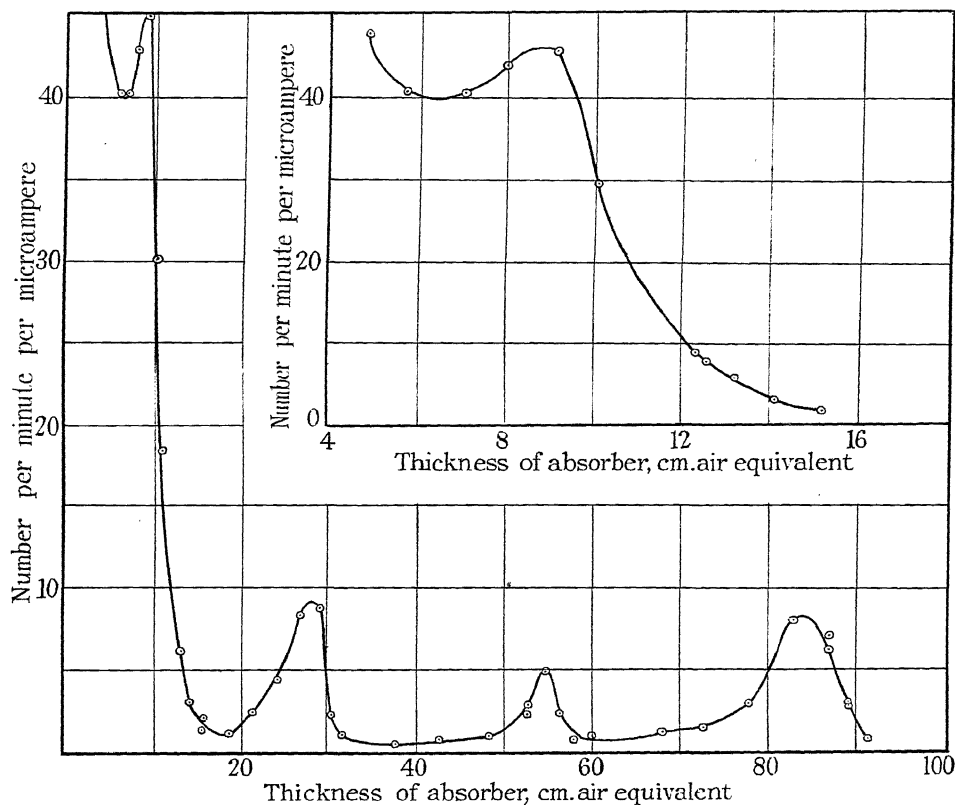


Figure 5.

should obtain a total value of  $9.3 \pm 0.5$  m.V. The 58 cm. group on the other hand would give a release of energy of 7.0 m.V. There is thus an uncertainty in the explanation of the proton groups. The discrepancies may, however, be due to a variation in the stopping power of mica for fast protons, since we have seen that considerable errors have been introduced in assuming its constancy for  $\alpha$ -particle velocities.

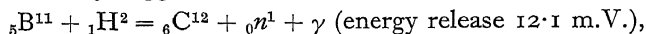
The proton groups of lower energy may be associated with the emission of part



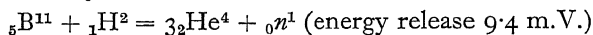
of the energy of the transmutation in the form of  $\gamma$ -rays. Lauritsen and Crane\* have reported that two groups of  $\gamma$ -rays are emitted from boron under diplon bombardment, the approximate energies being 2 m.V. and 4 m.V., one quantum being emitted for  $6 \times 10^7$  dions at 600 kV. acceleration potential, a yield of the same order of magnitude as that obtained for the proton emission in the experiments of Cockcroft and Walton.

(2) *Disintegrations leading to the emission of neutrons*

Lauritsen and Crane\* report the emission of neutrons from boron under diplon bombardment, the numbers at 900 kV. acceleration potential being about 1 for  $9 \times 10^6$  dions. They suggested that the reaction occurring was



although the possibility of the reaction

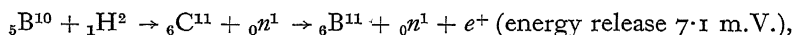


should not be excluded. The occurrence of such a reaction might complicate considerably the interpretation of the absorption curve for boron and it would be of the greatest interest to have separated sources of  $\text{B}^{10}$  and  $\text{B}^{11}$ .

Until measurements of neutron energy and such separated sources are available, however, it is not possible to be certain of the nature of the reaction.

(3) *Disintegrations leading to the emission of positrons*

The discovery by Curie and Joliot† that artificial radioactivity could be produced by  $\alpha$ -particle bombardment led immediately to the production of unstable isotopes by proton and diplon bombardment‡. Lauritsen and Crane have shown that positrons are emitted when boron is bombarded by dions, and suggest that the transmutations



take place. This reaction would thus give an alternative method of transmutation of one isotope into the next heavier.

Observations by Cockcroft, Gilbert and Walton on the decay period of the activity have given values for the half life varying from 18 to 25 minutes, the shorter period being shown by the gas driven off from the target by heating and by nuclei collected after recoil. This variation may be due to the presence of two periods, but further experiments are required. The emission of a heavy particle in the transmutation has been confirmed by measuring the recoil range of the radioactive nucleus and it has been shown that the radioactive gas can be condensed by liquid air, this being consistent with it being carbon monoxide or carbon dioxide.

The reaction leading to the formation of an unstable isotope seems to occur much more rarely than the reactions leading to the emission of a proton or of

\* This volume, p. 141.

† *Comptes Rendus*, 198, 254 (1934).

‡ Cockcroft, Gilbert and Walton, *Nature*, March 3, 1934; Lauritsen and Crane, *Phys. Rev.* March 15, 1934.

$\alpha$ -particles. Lauritsen and Crane report that about one positron is produced at 900 kV. for  $2 \times 10^9$  diplons in a target of boron oxide; Cockcroft, Gilbert and Walton have found that one positron would be produced at 550 kV. for  $4 \times 10^8$  diplons in a target of pure boron, an efficiency of the order of one-fortieth of that for proton emission. They find further that the activity produced by protons at 550 kV. is less than one four-hundredth of the activity produced by diplons, a result in conflict with a report of Lauritsen and Crane.

## II. 1. THE DISINTEGRATION OF CARBON BY PROTONS

When carbon is bombarded by protons, the emission of small numbers of  $\alpha$ -particles having a range of 2–3 cm. is observed. Particles of this range are, however, emitted from practically all elements under proton bombardment and they are most probably due to an impurity.

After bombardment by protons, however\*, carbon is observed to become radioactive, emitting positrons with a decay period of  $11 \pm 1$  minutes. It has been

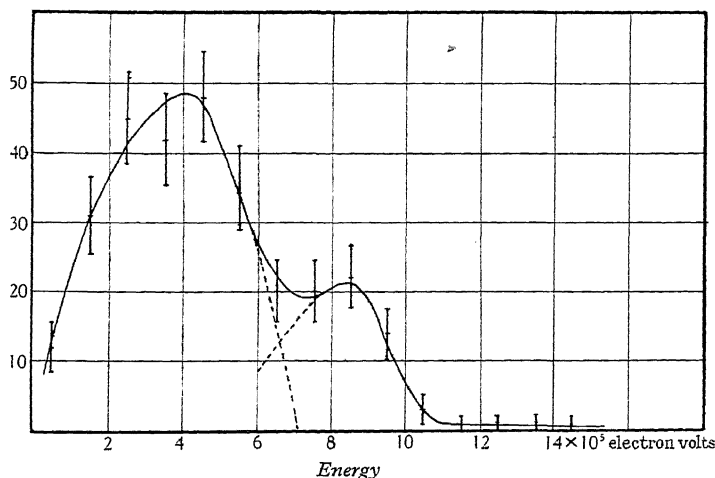


Figure 6.

suggested† that this effect is spurious and is due to the presence of diplons in the bombarding stream. This possibility seemed extremely unlikely since magnetic analysis was used to separate the protons and diplons. As a further test, however, Cockcroft, Gilbert and Walton bombarded lithium with the same beam of ions; the complete absence of 13 cm.  $\alpha$ -particles proved conclusively that there was less than 1 part in 2000 of diplons in the beam, whilst the activity produced by the proton beam is of the order of 10 per cent of that produced by the dipton beam of the same energy.

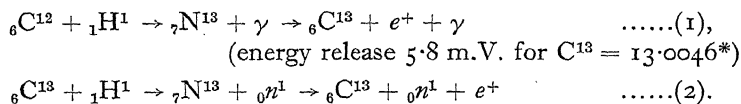
\* Cockcroft, Gilbert and Walton, *Nature*, *loc. cit.*

† Tuve, Hafstead and Dahl, *Phys. Rev.* 45, 902 (1934).

The energy spectrum of the positrons has been measured by the Wilson chamber with the results given in figure 6. It will be seen that the maximum energy is of the order of 1100 kV. The interpretation of the hump in the curve at 850 kV. is at present uncertain. It may be due to the experiments having been carried out before magnetic analysis was used so that our beam may have contained 10 per cent of diplons, the diplons and protons giving different energy distributions.

The absolute yield of the reaction has been measured roughly, and at 550 kV. proton energy it is one disintegration for  $5 \times 10^9$  protons.

Two possible reactions are suggested by the conservation of charge and mass:



Of these reactions, (2) seems unlikely, for it requires the neutron mass to be less than 1.0057, since the only available energy would arise from the change of a proton to a neutron plus a positive electron. The small relative abundance of the  $\text{C}^{13}$  isotope is another argument against its likelihood.

The first reaction is, on the other hand, energetically possible. It has been objected on theoretical grounds that the probability of such a reaction with the emission of the surplus energy in the form of radiation must be small. We have seen, however, that the probability of the reaction taking place is in fact small, being of the order of one-thousandth of that which would be expected for the emission of heavy particles.

## II. 2. THE DISINTEGRATION OF CARBON BY DIPLONS

### (1) *Disintegrations leading to the emission of protons*

Under dipton bombardment, carbon is observed to emit protons having a range of  $14.0 \pm 1$  cm. at 500 kV.†, and 18 cm. at 1.2 m.V.‡ No accurate determination of the yield is available but it is certainly not less than one disintegration for  $2 \times 10^8$  diplons at 600 kV.

Evidence for the emission of  $\gamma$ -rays under bombardment by 900 kV. diplons has been obtained by Lauritsen and Crane§, the absorption coefficient of the radiation being  $0.35 \text{ cm}^{-1}$  corresponding to an energy of the order of 3 m.V., one quantum being produced for about  $3 \times 10^8$  diplons at 900 kV., and for  $3 \times 10^9$  diplons at 700 kV.

Experiments on the disintegration of boron by  $\alpha$ -particles|| have shown that the  $\text{C}^{13}$  nucleus has an excited state at about 2.7 m.V. The  $\gamma$ -ray reported by Lauritsen and Crane may thus be associated with the transition of the nucleus from this

\* Mass from disintegration of  $\text{B}^{10}$  by  $\alpha$ -particles.

† Cockcroft and Walton, *Proc. R.S. loc. cit.*

‡ Lawrence, Livingston and Lewis, *Phys. Rev.* **44**, 56 (1933).

§ *Phys. Rev.* **45**, 346 (1934).

|| Chadwick, Constable and Pollard, *Proc. R.S.* **130**, 463 (1931); Duncanson, Miller and May, *Proc. Camb. Phil. Soc.* **30**, 549 (1934).

level to the ground state. We should then expect the ejection of the proton with an energy change of  $2.7 \pm 0.16$  m.V. to be followed by the emission of the  $\gamma$ -ray so that the total energy release would be 5.4 m.V. If we use the disintegration mass of  $C^{13}$ , we should expect an energy release of  $4.5 \pm 0.5$  m.V. If on the other hand we take the band-spectrum mass of  $C^{13}$  (13.0039), the energy release should be 5.2 m.V.

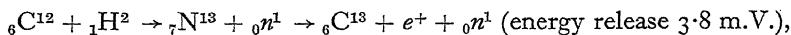
The range of the protons ejected from carbon is about 1 cm. less than the range of the protons resulting from the bombardment of heavy hydrogen by diplons\*. It seemed possible therefore that the protons from carbon might be due to the contamination of the target with heavy hydrogen from the bombarding stream. In this case, however, we ought to observe the short range  $H^3$  particles resulting from the  $D + D$  reaction in numbers equal to the 15 cm. protons. Our results show that although this is actually observed for heavy hydrogen targets, the number of short range particles from carbon is very much less than would be expected if the whole effect were due to contamination. We also find that the number of protons ejected increases very much more rapidly with voltage in the case of carbon plus diplons than in the case of a heavy hydrogen target plus diplons. Tuve, Hafstead and Dahl† have stated that the number of 14 cm. protons produced by a stream of diplons passing through  $CO_2$  gas is less than 1 in 400 of the number produced by the same stream passing through pure heavy hydrogen, and from this have inferred that the whole carbon effect is due to adsorbed heavy hydrogen. Under the conditions of their experiment, however, it would be expected that the yield for heavy hydrogen should be at least 400 times that from  $CO_2$  since they state that one disintegration is produced for several thousand diplons, so that no definite conclusion can be drawn from the experiment.

## (2) *The production of induced radioactivity by dipton bombardment of carbon*

After bombardment by diplons, carbon is observed to become radioactive and to emit positrons, the activity decaying with the same half life ( $11 \pm 1$  min.) as that observed in the case of carbon activated by protons.

Absorption measurements in aluminium have shown that the maximum energy of the positron spectrum is of the order of 1100 kV. and suggest that the minimum energy is greater than 100 kV.

It seems probable that the transmutation occurring is



the unstable isotope  $N^{13}$  transforming into  $C^{13}$  with the emission of a positron. Two experimental tests have been made on this reaction. The emission of a heavy particle in the primary reaction has been verified by measuring the recoil range of the radioactive nuclei. It was found that these nuclei would pass through one foil having a stopping power of 0.75 mm. but were stopped by two such foils. Their range lies therefore between 0.75 and 1.5 mm. and their energy between 150 and

\* Rutherford, Harteck and Oliphant, *Proc. R.S. A*, 144, 692 (1934).

† *Phys. Rev.* 45, 651 (1934).

350 kV.\* This is consistent with the view that a neutron having an energy of between 1.9 and 4.5 m.V. is emitted.

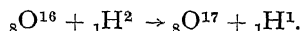
Experiments have also been made to determine the nature of the radioactive gas and have shown that after mixing with nitrogen the gas can be liquefied by passage through a trap cooled by liquid nitrogen boiling at 1 cm. pressure, but is not liquefied by passage through a trap cooled by liquid nitrogen at ordinary pressure. These results would be expected if the radioactive gas were nitrogen.

The yield of positrons obtained in this reaction is much smaller than the yield of protons in the reaction discussed in II. 2. (1), about 1 positron being produced for  $5 \times 10^8$  diplons at 550 kV.

### III. 1. THE DISINTEGRATION OF OXYGEN BY DIPLONS WITH PROTON EMISSION

The emission of protons having a range of  $8 \pm 1$  cm. from a target of oxidized tungsten bombarded by 500 kV. diplons has been observed by Cockcroft and Walton†, these protons not occurring when the target is cleaned by heating.

The proton energy is consistent with the reaction

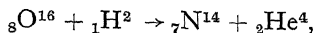


If we take the mass of  $\text{O}^{17}$  to be  $17.004 \pm 0.001$  (disintegration data) and assume that the kinetic energy of the diplon appears in the nuclei after the disintegration, then the kinetic energy to be expected in the proton is 2.0 m.V., corresponding to a range of 7 cm.

### III. 2. THE DISINTEGRATION OF OXYGEN WITH THE EMISSION OF $\alpha$ -PARTICLES

In the experiments described above, the emission of  $\alpha$ -particles having a range of  $2 \pm 0.5$  cm. was also observed from an oxidised tungsten target, these particles not being observed from the target after cleaning by heating.

The particles may result from the reaction



the kinetic energy expected being 2.9 m.V., corresponding to a range of 1.6 cm.

Further work is again required before this interpretation can be considered to be established.

### IV. THE DISINTEGRATION OF FLUORINE BY PROTONS

The emission of  $\alpha$ -particles in the bombardment of calcium fluoride was observed in the first experiments of Cockcroft and Walton, the range of the particles being determined approximately by scintillation methods as 3 cm. In later experi-

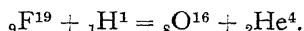
\* Blackett and Lees, *Proc. R.S.* 134, 670 (1931).

† *Loc. cit.*

ments, Rutherford and Oliphant\*, using a target of iron fluoride and a bombarding potential of 200 kV., obtained  $\alpha$ -particles having ranges up to 4 cm.

More recent experiments by Henderson, Livingston and Lawrence† have shown that at 675 kV. energy, two groups of  $\alpha$ -particles occur, one having a range of 3 cm. and the other having a range of 6 cm., this latter range increasing to 6.8 cm. as the proton energy is increased to 1.63 m.V. These authors state, without giving details of the proof, that the shorter range group is due to contamination by boron.

The most probable reaction to explain the observation is



If we take Aston's value for  $\text{F}^{19}$  ( $19.000 \pm 0.0015$ ) we should expect to obtain a mean  $\alpha$ -particle range of  $2.7 \pm 1$  cm. for zero proton energy. If the minimum  $\alpha$ -particle range is 6 cm. at 675 kV. proton energy, then the mass of  $\text{F}^{19}$  from the disintegration data would be 19.0025, a value more in accord with the disintegration data‡ and Bainbridge's mass of  $\text{Ne}^{22}$  than Aston's value.

## V. THE DISINTEGRATION OF HEAVIER ELEMENTS

In the first experiments of Cockcroft and Walton§ the emission of  $\alpha$ -particles was observed from most targets when bombarded by protons, these  $\alpha$ -particles having a common range of about 3 cm. At that time characteristic differences in the numbers of particles from different targets led to the belief that these effects were due to transmutations, although it was stated explicitly that they might well be due to impurities.

The emission of such particles from several of the heavier elements has since been shown|| to vary with the treatment of the target, suggesting that the whole of these effects are due to an impurity which may be boron or oxygen, although it has not yet been traced with certainty.

A similar phenomenon has been observed in the case of dipton bombardment¶, practically all elements emitting protons of range about 18 cm. This phenomenon was carefully studied by Cockcroft and Walton\*\*, who showed that the effects were due to thin films of carbon and heavy hydrogen, these elements giving large numbers of protons of about this range on dipton bombardment.

These two experiences indicate the particular importance of eliminating impurity effects in disintegration produced by protons and diplons. Whenever a particle range is close to a range coming from a very "active" element it will probably only be possible to settle the nature of the reaction by Wilson chamber methods or by measurements of range of higher precision than have hitherto been made.

\* *Proc. R.S.* **141**, 259 (1932).

† *Phys. Rev.* **46**, 38 (1934).

‡ Chadwick, Constable and Pollard, *Proc. R.S.* **130**, 463 n. (1931).

§ *Loc. cit.*

|| Rutherford and Oliphant, *Proc. R.S.* **141**, 200 (1934).

¶ Lawrence, Livingston and Lewis, *Phys. Rev.* **44**, 55 (1933).

\*\* *Proc. R.S. loc. cit.*

# VI. 1. THE EXCITATION FUNCTION FOR ARTIFICIAL DISINTEGRATIONS

It is of considerable importance to know accurately the rate at which the number of disintegrations varies with voltage for a series of elements and for different ions since such results may enable us to determine the interaction between different nuclear particles.

The chance that a particle will produce a disintegration on striking a thick target depends on four factors:

(i) The chance of a nuclear collision in unit length of path, this being given by  $N\sigma$ ,  $N$  being the number of nuclei per unit volume and  $\sigma$  the "effective nuclear collision cross-section." If we assume that particles having angular momenta about the nucleus less than  $\hbar/2\pi$  have an effective collision, we reach the result that the effective cross-section is  $\lambda^2/4\pi$ , where  $\lambda$  is the de Broglie wave-length of the particle\*, the cross-section then varying inversely as the energy of the particle. At the Solvay Conference (1933) some discussion took place as to the validity of this assumption, but it seems now to be agreed that it is correct for protons of the energies normally used.

(ii) The range of the particle in the target. This range is obtained from the results of Blackett and Lees† for protons up to 34 mm. range and from the calculations of Duncanson‡ for higher ranges.

(iii) The chance of the particle penetrating the nuclear potential barrier. This chance is given by the Gamow factor

$$G = \exp. \left\{ -\frac{e^2}{\hbar} \sqrt{(2m)} \cdot \frac{zeZ}{\sqrt{E^*}} (2u - \sin 2u) \right\}$$

where

$$\cos^2 u = \frac{r_0 E^*}{zeZe^2}$$

and

$$E^* = \frac{mM}{m+M} E.$$

Here  $e$  is the electronic charge,  $m$  the mass of the bombarding particle,  $M$  the mass of the nucleus bombarded,  $ze$  the charge on the bombarding particle,  $Z$  the atomic number of the nucleus bombarded,  $E$  the energy of the bombarding particle in ergs. The calculation assumes that the field of force outside the nucleus increases according to the inverse square law until a distance  $r_0$  is reached from the centre of the nucleus and that it then changes to an attractive field.  $r_0$  thus determines the maximum of the potential barrier round the nucleus and  $u$  tends to zero as the particle energy tends to equality with this maximum.

The value of  $r_0$  must ultimately be fixed by experiment. For  $\alpha$ -particles it is given approximately by  $1.75 \times 10^{-13} Z^{\frac{1}{2}}$ , whilst experimental data for protons suggest the value  $3.7 \times 10^{-13} Z^{\frac{1}{2}}$  for light nuclei. In the absence of data for diatoms

\* Beck, *Kernbau und Quantenmechanik*, p. 380.

† *Proc. Camb. Phil. Soc.* 30, 102 (1934).

‡ *Loc. cit.*

the same value will be used. Using this value a convenient approximate expression for  $G$  is

$$_{10} - \left( A \frac{Z}{\sqrt{E_p}} - BZ^{\frac{1}{2}} \right)$$

the values of  $A$  and  $B$  being given below—

	$B$	
Protons	0.43	0.87
Diplons	0.61	1.24
$\alpha$ -particles	1.72	1.7

—and  $E$  being measured in millions of volts.

(iv) The chance that disintegration will occur after penetration of the potential barrier has taken place. This chance must depend on the available energy, on the spin of the different nuclear particles\*, on the distribution of momentum between the different particles after the break up and on the chance of the particles escaping through the potential barrier. At present it is only possible to estimate qualitatively the effect of these factors, and it seems likely that a satisfactory theory must await more complete experimental data.

## VI. 2. EXPERIMENTAL FIGURES

The experimental figures for the voltage variation available at present are subject to considerable uncertainty owing to most of the earlier experiments having been carried out without magnetic analysis of the ion beam, the relative proportion of protons and molecular ions being thus uncertain. The figures are, however, good enough to enable a rough comparison to be made with theory.

In Table 1 figures are given for the relative number of disintegrations produced by a fixed number of bombarding ions at different accelerating voltages. In interpreting the table it should be borne in mind that the effective voltage for disintegration is  $\frac{mM}{m+M}$  times the accelerating voltage, this correction being small except in the diplogen-diplogen reaction.

Table 1

Voltage kV.	Reaction						
	$D^2 + D^2 \rightarrow$ ${}_1H^1 + {}_1H^3$	$Li^7 + H^1 \rightarrow$ ${}_2He^4$	$Li^6 + D^2 \rightarrow$ ${}_2He^4$	$Li^6 + D^2 \rightarrow$ $Li^7 + H^1$	$B^{11} + H^1 \rightarrow$ ${}_3He^4$	$B^{10} + D^2 \rightarrow$ ${}_3He^4$	$C^{12} + D^2$
600	—	—	1.0	1.0	1.0	1.0	1.0
500	—	0.6	0.6	0.6	0.68	0.38	0.23
400	—	0.33	0.34	0.24	0.38	0.066	0.08
300	—	0.10	0.15	0.10	0.16	0.013	0.015
200	—	—	—	—	—	—	—
160	1.0	1.0	1.0	—	1.0	—	—
130	0.6	0.47	0.36	—	0.36	—	—
100	0.33	0.13	0.005	—	0.029	—	—
80	0.14	0.08	—	—	< 0.001	—	—



From these figures we can draw the following conclusions:

(i) Comparing the dipion-dipion with the dipion-lithium reaction at low voltages we see that the numbers decrease more rapidly with decreasing voltage in the case of lithium than in that of heavy hydrogen, in spite of the fact that the "reduced" voltages for dipions are one-half the applied voltages.

(ii) Comparison of the figures for lithium, boron, and carbon between 300 and 600 kV. shows that for higher atomic numbers the numbers fall off much more rapidly with decreasing voltage.

(iii) Comparison of the reactions of lithium and boron with protons and dipions shows that the numbers fall off much more rapidly for dipions than for protons.

These results are evidently in qualitative agreement with Gamow's theory, for between 300 and 600 kV.  $G$  varies by  $10^{0.22}$  for protons and by  $10^{0.38}$  for dipions, so that the more rapid variation with voltage for dipions as compared with protons and for higher atomic number is to be expected.

### VI. 3. HEIGHT OF POTENTIAL BARRIERS

Although some information about the heights of potential barriers around nuclei may be obtained from experiments with particles of low energy, we can obtain much more direct information by comparing the number of disintegrations with the range of the particle for different voltages. For this purpose it is advantageous to have results for as high energy particles as possible. In table 2 are given the experimental results of Rutherford and Oliphant and of Lawrence and his co-workers for heavy hydrogen, lithium, boron and fluorine\*.

Table 2

Voltage kV.	D + D		Li <sup>7</sup> + H <sup>1</sup>		B + H <sup>1</sup>		F + H <sup>1</sup>	
	Relative range	Relative numbers	Relative range	Relative numbers	Relative range	Relative numbers	Relative range	Relative numbers
1600	—	—	—	—	—	—	I	I
1300	—	—	—	—	—	—	0.74	0.31
1000	—	—	I	I	I	I	0.52	0.047
800	—	—	0.74	0.66	0.74	0.63	—	—
600	—	—	0.49	0.39	0.49	0.34	—	—
400	—	—	0.28	0.15	0.28	0.13	—	—
160	I	I	—	—	—	—	—	—
130	0.86	0.66	—	—	—	—	—	—
100	0.68	0.30	—	—	—	—	—	—

From these results we deduce that the change in the number of disintegrations is not proportional to the change in range in any of the intervals covered, but that the numbers are approaching proportionality in the case of lithium and boron bombarded by protons of energies between 800 and 1000 kV. and for heavy hydrogen bombarded by dipions at 160 kV. Allowing for the correction to effective voltages, we may therefore state that the top of the potential barrier for dipions on heavy hydrogen is greater than 80 kV.; for protons on lithium and boron is greater than

\* *Phys. Rev.* 43, 98, 304 (1933); 46, 38 (1934).

700 kV. and probably of the order of 1 m.V.; and for protons on fluorine considerably greater than 1600 kV.

These figures are lower than the experimental figures for the heights of potential barriers for  $\alpha$ -particles given in table 3; it should be remembered of course that these potentials are double the potential which would be effective for a singly charged particle.

Table 3\*

Element	Li	Be	B	C	F
Height of barrier (m.V.)	2.8	3.5	3.6	3.7	5.0

If therefore the field is to be treated as Coulombian up to a distance  $r_0$ , the values of  $r_0$  must be larger than for  $\alpha$ -particles and for lithium would be about  $5.3 \times 10^{-13}$  instead of the  $\alpha$ -particle value  $2.5 \times 10^{-13}$ . This higher value is on the other hand of the same order as is required by experiments on the scattering of  $\alpha$ -particles in hydrogen†, where a value of  $r_0$  for helium of  $4.5 \times 10^{-13}$  is found to fit the results best.

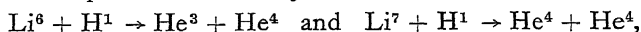
#### VI. 4. THE CHANCE OF DISINTEGRATION AFTER PENETRATION OF THE BARRIER

The increase in the number of disintegrations of lithium due to an increase in proton energy from 800 to 1000 kV. is due almost entirely to the increased range of the proton, so that all the protons making a nuclear collision enter the nucleus. The chance of an effective nuclear collision due to the increased range of 0.7 cm. is easily calculated to be 1 in 20,000, taking the nuclear cross-section as  $7.2 \times 10^{-25}$  cm<sup>2</sup>. The increase in the number of disintegrations observed is, on the other hand, 1 for  $2 \times 10^7$  protons. It follows therefore that only 1 proton in 1000 entering the nucleus is effective in producing a disintegration.

A similar argument may be applied to boron and we again find that the chance of a proton producing a disintegration after entering the nucleus is of the order of 1 in 1000.

In the case of heavy hydrogen bombarded by diplons, however, the absolute yield is very much larger, only  $10^6$  100-kV. diplons being required to produce one disintegration in heavy hydrogen gas, and we can place a lower limit of 1 in 20 to the chance of disintegration after entering.

We can also compare the absolute yield of the reactions



and find that the first reaction occurs at least thirty times as frequently as the second for the same proton energies.

As has been pointed out by Goldhaber and Beck these differences in the yield can be accounted for qualitatively by a consideration of the changes of angular momentum which have to take place in the process.

\* Chadwick and Feather, this volume, p. 103.

† Taylor, *Proc. R.S.* 136, 605 (1933).

## GAMMA-RAYS FROM ARTIFICIALLY PRODUCED NUCLEAR TRANSMUTATIONS

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*ABSTRACT.* Gamma-rays have been found resulting from the following processes: lithium and fluorine bombarded with protons; beryllium, boron and carbon bombarded with deuterons. Attempts have been made to determine the quantum energies by means of absorption measurements in lead and in copper, and also by means of cloud chamber photographs of the recoil electrons and electron pairs ejected from a lead plate by the radiation. Counts of the relative numbers of electron pairs and of single negative recoil electrons produced by 12 m.e.V. and by 5.4 m.e.V. radiation have been made, and found to agree satisfactorily with the theoretical predictions of Oppenheimer and of Bethe and Heitler. Finally, a list of the excitation levels which have been found by the study of  $\gamma$ -ray emission from the various light nuclei is given, and this includes evidence for one, and possibly two, excitation levels in the  $\alpha$ -particle.

### § 1. INTRODUCTION

THE fact that many of the natural radioactive elements emit monochromatic  $\gamma$ -rays, in addition to  $\alpha$ -particles of definite ranges, is strong evidence that the nuclear energy is quantized in a manner similar to that of the extranuclear electrons. This point of similarity to the extranuclear structure early suggested that it might be possible to excite any nucleus if it could be subjected to a disturbance of sufficient violence. Beginning in 1913, at the instigation of Rutherford and Chadwick, attempts were made to observe the  $\gamma$ -rays which would be expected to result from such excitation, and many investigators reported the finding of radiation when a number of elements were bombarded by swift  $\alpha$ -particles, but these results were usually spurious or explicable as extranuclear phenomena. It was not until 1930 that conclusive evidence was offered for the production of  $\gamma$ -rays by  $\alpha$ -particle bombardment.

The first successful experiments of this kind were those of Bothe and Becker<sup>(1)</sup>, who demonstrated that high energy  $\gamma$ -rays were produced when lithium, beryllium, boron and fluorine were bombarded with the  $\alpha$ -particles from polonium. By means of coincidence Geiger counters they<sup>(2)</sup> were able to measure the range of the recoil electrons, and thus to arrive at an estimate of the quantum energy of the  $\gamma$ -rays, which came out to be approximately 5 m.e.V. (million electron volts) for the beryllium and 3 m.e.V. for the boron. In addition, they attempted to measure the absorption coefficient of the  $\gamma$ -rays in lead and in iron, but found values which were very much

lower than those to be expected for the above quantum energies. This discrepancy may have been caused in part by the neutrons which were later shown by Chadwick<sup>(3)</sup> to be present in large numbers. Subsequently, Curie and Joliot<sup>(4)</sup> and others verified these results. Webster<sup>(5)</sup> found that the  $\gamma$ -ray produced when lithium was bombarded with the  $\alpha$ -particles from polonium had a quantum energy of approximately 0.6 m.e.V. It is interesting that in the case of beryllium no sharp lower limit was found for the energy of  $\alpha$ -particles which could produce  $\gamma$ -rays, while in the cases of lithium and boron there were definite thresholds at 3 and 2 m.e.V. respectively, the reason for which will become evident at a later point in this discussion.

## § 2. THE USE OF ARTIFICIALLY ACCELERATED PARTICLES

Until quite recently the only particles available for producing nuclear transmutations were the fast  $\alpha$ -particles from natural radioactive elements, but to these have now been added a number of artificially accelerated particles, the most important of which are protons, deutons, and helium ions. The kinetic energy of such particles is still far short of that available with  $\alpha$ -particles, but this is at least partly compensated for by the much larger number of particles obtainable.

The first successful attempt to produce nuclear transformations by means of artificially accelerated particles was that of Cockcroft and Walton<sup>(6)</sup> who found that protons with quite moderate energies were effective in producing transmutations of a number of the lighter elements. Lewis, Livingston and Lawrence<sup>(7)</sup> obtained evidence for the disintegration of many more elements by means of artificially accelerated deuterons, whilst Crane, Lauritsen and Soltan<sup>(8)</sup> succeeded in producing transmutations yielding neutrons by means of artificially accelerated helium ions.

With these discoveries a new and large field has been thrown open in which to search for  $\gamma$ -rays and for excitation levels in the various nuclei. In the investigation of  $\gamma$ -rays the problem of obtaining sufficient intensity is in general more serious than in the counting of  $\alpha$ -particles or protons given off in the same reaction, and it is often further complicated by the presence of neutrons, which cannot conveniently be filtered out, and which are of roughly the same effectiveness as photons in producing ionization. For example, in order to produce, at a distance of 10 cm. from the source, an effect in an ionization chamber equal to the usual background due to cosmic ray, etc., it is necessary to produce about  $10^4$  photons per sec., and for accurate absorption measurements, a considerably greater intensity is desirable. By working with an ion beam of from 10 to 30  $\mu$ A., and usually at 0.9 m.e.V.<sup>(9)</sup>, we have been able to obtain sufficient intensities for the investigation of the resulting  $\gamma$ -rays in some of the more efficient of the disintegration processes.

For the purpose of searching for  $\gamma$ -rays in the various transmutations, and for measuring their absorption coefficients, we have used a sensitive cantilever type electroscop, enclosed in an air-filled ionization chamber of about 150 c.c. volume and at atmospheric pressure. This was placed at a distance of from 10 to 30 cm. from the target, and shielded so that only radiation coming from the target could be recorded. This arrangement permitted the use of absorbing materials up to

15 cm. in thickness. In those instances in which the  $\gamma$ -rays were accompanied by neutrons, we have found it possible to separate the two effects by measuring the absorption of the mixed radiation, both in lead and in paraffin, using in each case a paraffin and a lead-lined ionization chamber. The paraffin-lined chamber is more than twice as sensitive to neutrons as the lead-lined chamber, and in general less sensitive to  $\gamma$ -rays than the lead-lined chamber, and the absorption coefficients of the two kinds of radiation are of course very different in lead and in paraffin. As

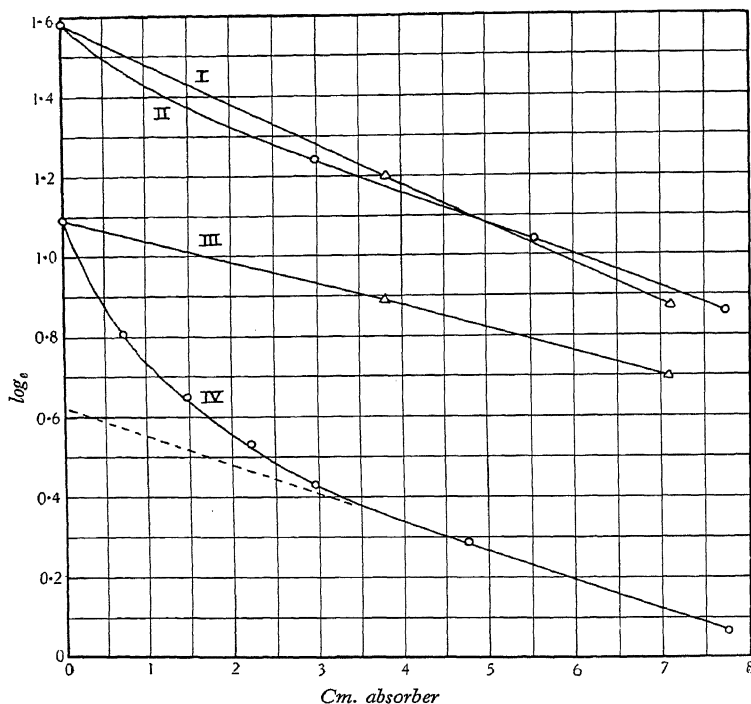


Figure 1. Absorption of the beryllium-deuteron radiation. I, paraffin-lined chamber, paraffin absorber; II, paraffin-lined chamber, lead absorber; III, lead-lined chamber, paraffin absorber; IV, lead-lined chamber, lead absorber.

an example, the four absorption curves obtained in this way, in the case of beryllium bombarded with deuterons<sup>(10)</sup>, are shown in figure 1.

Let us consider first the curves (II and IV) for the lead absorber, at thicknesses greater than 4 cm. The slope is the same for the lead and the paraffin chambers, indicating that the radiation is, after this filtration, of a single type, either entirely neutrons or entirely  $\gamma$ -rays. The large displacement of curve II (paraffin chamber) above curve IV (lead chamber) shows clearly that it is in fact composed of neutrons. The slope of curves II and IV beyond 4 cm. absorption is therefore taken to be the absorption coefficient for the neutrons in lead. At thicknesses of absorber less than 4 cm., curve IV shows a steep rise, which clearly indicates the

presence of a component of radiation which is much more absorbable than the neutrons, and which is almost entirely screened out by 4 cm. of lead. That this component is  $\gamma$ -radiation, is indicated by the fact that it shows up very much more in the lead chamber curve than in the corresponding paraffin chamber curve. By extending the straight part of curve IV backward, as indicated by the dotted line in figure 1, we can determine the intensity contributed by neutrons alone, for absorbers less than 4 cm. The difference between the total intensity and the intensity repre-

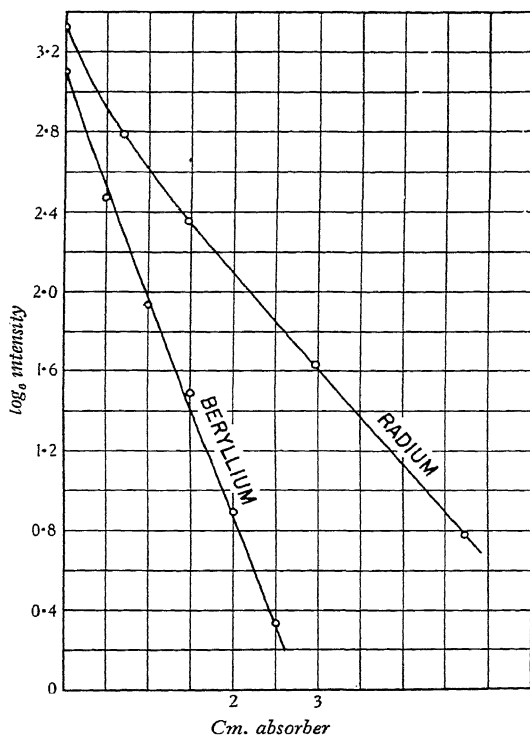


Figure 2. Absorption curve of the beryllium-deuteron  $\gamma$ -rays, with an absorption curve of radium  $\gamma$ -rays taken under the same experimental conditions.

sented by the dotted line should then be just the intensity due to the  $\gamma$ -rays. Since all the curves are on a logarithmic scale, the intensity of  $\gamma$ -rays will be the difference between the antilogarithms of corresponding points on curve IV and the dotted line. The intensity of  $\gamma$ -rays thus obtained, as a function of thickness of absorber, is plotted on a logarithmic scale in figure 2. The fact that the plot is a straight line suggests that the gamma radiation is monochromatic. Its absorption coefficient is  $1.2 \text{ cm}^{-1}$ , corresponding to a quantum energy of about 0.7 m.e.V. Using this technique we found  $\gamma$ -rays in the following cases: lithium bombarded with protons; beryllium, boron, and carbon bombarded with deuterons. These  $\gamma$ -rays were found to have absorption coefficients in lead of 0.55, 1.2, 0.62 and 0.35 respectively.

be masked by the slower electrons, and by the softened radiation resulting from the 12 m.e.V. component.

The absorption coefficient for the radiation in lead (figure 3) corresponds to about 6.9 m.e.V., and this is not inconsistent with a composite radiation consisting of roughly equal intensities of 12 and 4 m.e.V. components, as suggested by the electron spectrum. No exact comparison is possible, since the relative intensities are not accurately known.

It is seen in figures 4 and 5 that the high energy limit of the negative electrons is roughly 1 m.e.V. higher than that of the positive electrons, and this is consistent with the theory of pair formation. On the assumption that the number of negatives

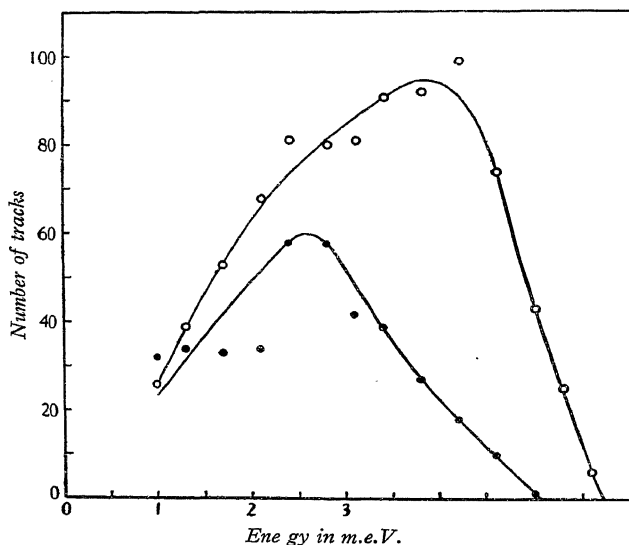


Figure 4. Energy spectra of the negative and positive electrons ejected from a thick lead plate by the  $\gamma$ -radiation from fluorine bombarded with protons. Circles indicate negative electrons and dots indicate positive electrons. Each point represents the number of electron tracks in a 0.7 m.e.V. energy interval.

belonging to pairs is equal to the number of positives, and that the positives and negatives resulting from pairs have essentially the same initial energy spectrum, we can subtract the number of positives from the total number of negatives to find the number of negatives which do not belong to pairs. To obtain the correct ratio of the number of pairs formed in a given volume of lead to the number of single negatives, we must apply a correction for the difference in the average range in lead of members of pairs and of single negatives. The average energy of a member of a pair is somewhat less than half that of a photoelectron or a forwardly directed Compton recoil electron, since the energy of the quantum must be divided between the two members of the pair. In this energy region, the Compton recoil electrons are nearly all forwardly directed and have energies near the maximum. A correction factor to com-

pensate for the greater average range of the Compton electrons is therefore necessary. It is indicated by the recent work of Bethe and Heitler<sup>(14)</sup> that in this energy region the range of electrons in lead does not increase in proportion to the energy, owing to the rapidly increasing probability of large radiative energy losses with the accompanying large angle scattering. Using their theoretical results we find average ranges of 2.6 mm. and 1.9 mm. for the Compton and pair electrons, respectively, from the 5.4 m.e.V. fluorine radiation. The ratio of the pair and Klein-Nishina absorption coefficients for this radiation computed from our experimental results is 1.25, in good agreement with the ratio 1.15 given by Bethe and Heitler. In the case

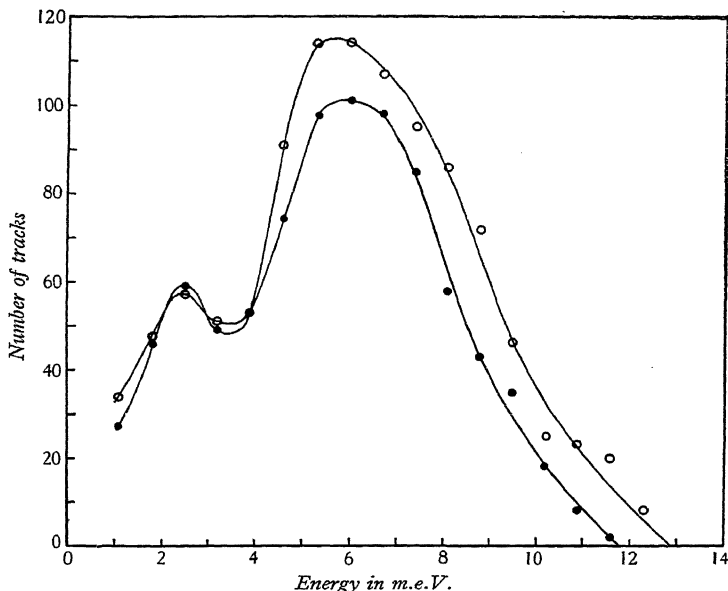


Figure 5. Energy spectra of the negative and positive electrons ejected from a thick lead plate by the  $\gamma$ -radiation from lithium bombarded with protons. Circles indicate negative electrons and dots indicate positive electrons. Each point represents the number of electron tracks in a 1.4 m.e.V. energy interval.

of the 12 m.e.V. lithium radiation the average range of the pairs is greater than 3 mm., the thickness of the lead absorber used. However, the glass wall and other materials between the absorber and the source were equivalent to an additional millimetre of lead in producing Compton electrons. Taking these facts into account we obtain 6.7 as the ratio of pair to Klein-Nishina absorption. This is seen to be somewhat higher than the theoretical ratio of 5 which is obtained from figure 3.

The shape of the high energy side of the observed positive electron spectrum is well accounted for if we assume that when a pair is produced, the energy of the quantum is most likely to be shared equally between the positive and negative electrons, and that the probability of unequal division of energy decreases roughly linearly with the departure from equality until the probability that one member



receives all of the energy is practically zero. The recent theoretical calculations of Bethe and Heitler<sup>(14)</sup> predict in this energy range a distribution which is slightly different from this, in that it has a rather broad maximum for the probability of nearly equal division of the energy between the two members of a pair. Such a distribution agrees equally well with the available experimental data. That the curve drops off on the low energy side is due to the fact that many of the electrons originating below the surface fail to come out because of the high probability of large angle scattering and large energy loss in the lead. For the same reason we must expect that only comparatively rarely will both members of a pair be observed when thick lead is used. Although we have observed relatively few pairs in our experiments with thick lead, yet in preliminary observations using thin lead, pairs are observed relatively much more frequently.

#### § 4. ORIGIN OF THE $\gamma$ -RAYS

Returning to the question of the emission of  $\gamma$ -rays during nuclear transmutations, a very important consideration is the identification of the particular nucleus or product of the transmutation which emits the  $\gamma$ -ray, and in which the quantum energy of the  $\gamma$ -ray therefore represents a quantized excitation level. We may perhaps speculate as to the course of events leading to the emission of a  $\gamma$ -ray as follows. The bombarding particle penetrates the potential barrier of the bombarded nucleus, resulting in a temporary aggregate of particles, which may contain all the ingredients of a normal nucleus, but the amount of energy contained will in general not be the right amount to satisfy a quantized energy state. The probability of its dropping from such an arbitrary energy state to a stable energy state by emitting radiation should, according to theory, be extremely small, and no example of it has yet been established experimentally. The actual result is that it splits up immediately into two or more new particles, stable or excited, the excess energy being carried away in the form of kinetic energy of the new particles, this being divided among them in such a way that momentum is conserved. Where several modes of splitting up are possible, all of them will presumably occur, but with different probabilities. So far we have said nothing of the case in which there is too little energy to form new particles—obviously here the result would be simply a return to the original two particles. Where the energy released in the transformation is sufficient, it is reasonable to think that one or more of the newly formed particles would sometimes be formed in an excited state and subsequently fall to its normal state with the emission of a  $\gamma$ -ray of discrete energy. This amount of energy would then appear as a difference in kinetic energy of two groups of disintegration particles, and it is indeed in this way that excitation levels in some of the nuclei were first discovered.

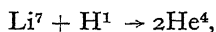
As a consequence of the above argument it seems reasonable to believe that in any transmutation, an observed monochromatic  $\gamma$ -ray is characteristic of one of the final products, as is well known for the case of natural radioactive decompositions. Where the same final product can be formed out of different combinations of ingredients, we might expect to find the same  $\gamma$ -ray, providing, always, that the

available energy is sufficient. Several experimental examples are already known which give strong support to this hypothesis. These are the formation of  $C^{13}$  out of  $B^{10} + He^4$  and  $C^{12} + H^2$ , the formation of  $B^{10}$  out of  $Li^7 + He^4$  and  $Be^9 + H^2$  and the formation of  $C^{12}$  out of  $Be^9 + He^4$  and  $B^{11} + H^2$ . These examples will be considered in detail below, and it will be seen that the quantum energy of the observed  $\gamma$ -ray is in each instance independent of the way in which the final product is formed, and is therefore presumably to be associated with an excitation level in the final product.

## § 5. ENERGY LEVELS IN THE VARIOUS NUCLEI

### *He<sup>4</sup> and He<sup>3</sup>*

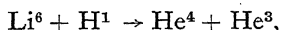
The first nucleus to be considered is the  $\alpha$ -particle, and this is one of the most important, since it is thought to be a common constituent of all the heavier nuclei, and is one of the most common products of nuclear transformations. By bombarding lithium with protons, as discussed in a previous section, we have obtained  $\gamma$ -rays of 12 m.e.V. and 4 m.e.V. energy, which we believe constitute evidence for one, and possibly two, excitation levels in the  $\alpha$ -particle. The 12 m.e.V. component we must ascribe to the reaction



because this appears to be the only reaction involving lithium and protons in which sufficient energy is released. That such strong radiation could be emitted in the impact of the protons on the lithium nuclei seems very improbable, both from theoretical considerations and from the experimental data at present available, though a small probability for the emission of radiation during the impact cannot be excluded. Presumably then the only possible source of the radiation is the final product,  $He^4$ .

It is more difficult to account for the 4 m.e.V. radiation arising from lithium bombarded with protons. We have not observed it in other reactions in which  $\alpha$ -particles are given off with more than 4 and less than 12 m.e.V. energy, as in beryllium, boron and fluorine bombarded with protons. Two suggestions as to its origin can be made, which are not in disagreement with these data. It could be due to an excitation level in  $He^3$ , or it could be due to an additional level in the  $\alpha$ -particle, lying above the 12 m.e.V. level already discussed.

That  $He^3$  is a possible product has been shown by Oliphant, Kinsey and Rutherford<sup>(19)</sup> who have observed its production in the reaction



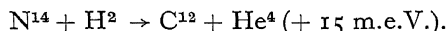
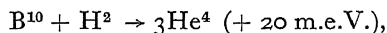
and have given 7 and 12 mm. as the ranges of the particles, when the energy contributed by the bombarding protons is 0.2 m.e.V. In our experiment, sufficient energy would be available to excite the  $He^3$  to 4 m.e.V., but there would be very little energy left to appear in the form of kinetic energy of the two particles, and hence they would not be easy to observe. The only other reaction from which  $He^3$  is known to be a product is



but here only about 2.5 m.e.V. of energy is available and we should therefore not expect to find the 4 m.e.V.  $\gamma$ -rays unless deuterons of very high energy were used.

If, on the other hand, we ascribe the 4 m.e.V.  $\gamma$ -ray to a second level in the  $\alpha$ -particle, we must assume that it lies above the 12 m.e.V. level, in order to account for the fact that it is not observed in processes where more than 4 but less than 12 m.e.V. are available. The  $\alpha$ -particle could then, in the case of lithium, appear in a state excited to 16 m.e.V. and could emit successively a 4 and a 12 m.e.V. quantum. In this case the  $\alpha$ -particles would each have less than 1 m.e.V. (less than 3 mm. range), and would be difficult to observe. If only the 12 m.e.V.  $\gamma$ -ray were emitted, the  $\alpha$ -particles would have about 1 cm. range and might correspond to the 9 mm. particles reported by Kirchner and Neuert<sup>(20)</sup>.

If our speculation as to the origin of the 12 m.e.V.  $\gamma$ -ray is correct, there should be the possibility of finding the same  $\gamma$ -ray in several other accessible processes in which  $\alpha$ -particles are given off with high energy. This would be the case, for example, when boron and nitrogen are bombarded by deuterons, the reactions being

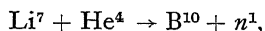


Having a sufficient amount of energy available, however, may not be the only condition which must be satisfied to make possible the excitation of the resulting  $\alpha$ -particle to a particular level.

Experiments are now under way to determine, by means of a Wilson cloud chamber, the energy spectra of recoil electrons due to boron and nitrogen disintegrated by deuterons, both of which should yield more information concerning the possibility of an excitation level in the  $\alpha$ -particle.

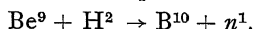
#### *B<sup>10</sup>*

Webster<sup>(5)</sup> has measured the absorption coefficient of the  $\gamma$ -rays emitted when lithium is bombarded with fast  $\alpha$ -particles and found the quantum energy to be  $0.6 \pm 0.1$  m.e.V. The reaction is assumed to be



and is, from a consideration of the masses involved, endothermic by 3 m.e.V. This is in accordance with the experiments of Curie and Joliot<sup>(21)</sup>, who found that  $\gamma$ -rays could be observed only if the bombarding  $\alpha$ -particles had more than 3 m.e.V., and that neutrons could be observed in addition to the  $\gamma$ -rays if the  $\alpha$ -particles had more than 5 m.e.V.

Another reaction which gives  $\text{B}^{10}$  as a product is

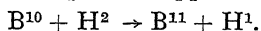


We have measured the absorption coefficient of the  $\gamma$ -rays from this process and have estimated that the quantum energy is about 0.7 m.e.V.<sup>(10, 12)</sup>. This is in good agreement with the results of Webster and indicates a level of that energy in  $\text{B}^{10}$ .

#### *B<sup>11</sup>*

Cockcroft and Walton<sup>(22)</sup> have reported that when boron is bombarded with

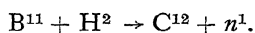
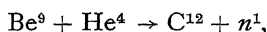
deutons, three groups of protons are emitted, of ranges 31, 58 and 92 cm. The only reaction which can account for the protons appears to be



Calculating the energy of the proton from the masses of the atoms involved, on the assumption that no  $\gamma$ -ray is emitted, and using 0.5 m.e.V. for the energy of the bombarding deuteron, we obtain 8.7 m.e.V., which corresponds to just 90 cm. range. Since this is the maximum range of the protons actually observed, it appears that the reaction assumed above is the correct one. On this assumption the 58 and 31 cm. ranges represent protons emitted together with  $\gamma$ -rays of 2 and 4 m.e.V. respectively. Judging from the intensities of the proton groups, the 4 m.e.V.  $\gamma$ -ray component is about twice as strong as the 2 m.e.V. component. In our cloud chamber studies of the radiation resulting from boron bombarded with deuterons<sup>(23)</sup>, we have observed  $\gamma$ -rays having components of about 2 and 4 m.e.V. in the above intensity ratio, in addition to other components which can be accounted for by reactions not giving  $\text{B}^{11}$  as a product.

### $\text{C}^{12}$

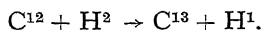
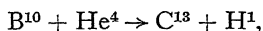
Two reactions in which  $\text{C}^{12}$  is produced are



In the first of these reactions, Bothe and Becker<sup>(2)</sup> have observed a  $\gamma$ -ray of 5 m.e.V. energy by means of coincidence Geiger counters. We have bombarded boron ( $\text{B}^{10}$  and  $\text{B}^{11}$ ) with deuterons and have obtained  $\gamma$ -rays having a strong component at about 5.5 m.e.V., together with the 2 and 4 m.e.V. components discussed in the preceding paragraph, and a weak component of considerably greater energy than 5.5 m.e.V. It is possible that the high energy component arises from the formation of  $\alpha$ -particles from  $\text{B}^{10} + \text{H}^2$ , although many more tracks will be required to determine its exact energy. The 5.5 m.e.V. component, however, checks very well with that found by Bothe and Becker, and it seems reasonable to assume that this is due in both cases to an excitation level in  $\text{C}^{12}$ .

### $\text{C}^{13}$

Two reactions have been studied which lead to the production of  $\text{C}^{13}$ , namely,

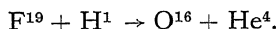


As a result of bombarding boron with  $\alpha$ -particles, Bothe and Becker<sup>2</sup> observed  $\gamma$ -rays and found by the method of coincidence Geiger counters, that the quantum energy was a little over 3 m.e.V. They found further that the energies of the protons which were emitted fell into two groups differing in energy by that amount, and that the maximum energy of the protons was in agreement with the amount of energy to be expected in the assumed reaction. We<sup>(13)</sup> have found a  $\gamma$ -ray resulting from the bombardment of carbon with deuterons and have found, by means of absorption measurements, that its quantum energy lies between 3 and 3.5 m.e.V.

Protons have been observed<sup>(22, 24)</sup>, resulting from carbon bombarded with deuterons, but so far only one energy group has been found. A calculation of the amount of energy available in the reaction indicates that the observed group of protons is composed of those which are emitted, together with the 3 m.e.V.  $\gamma$ -ray. It is only rarely, therefore, that the reaction takes place without the emission of a  $\gamma$ -ray.

### $O^{16}$

When fluorine is bombarded with protons the reaction which is supposed to take place is



The available energy is about 8 m.e.V. plus the bombarding energy. Henderson, Livingston and Lawrence<sup>(25)</sup> have observed  $\alpha$ -particles of between 6 and 7 cm. range, and McMillan<sup>(15)</sup> has observed  $\gamma$ -rays of about 5.5 m.e.V. We have confirmed McMillan's observation, both by absorption measurements and by cloud chamber photographs of the recoil electrons<sup>(17)</sup>. The cloud chamber method is probably the most reliable, and gives 5.4 m.e.V. as the quantum energy. It is quite certain that this represents a level in  $O^{16}$  since, as we have seen,  $He^4$  probably has no level in this energy region. From McMillan's observation of the relative number of  $\gamma$ -rays and 6 to 7 cm.  $\alpha$ -particles, it appears that in about 6 out of 7 disintegrations the  $O^{16}$  comes off excited. Under these circumstances there is very little energy left for the  $\alpha$ -particle, and it has so far not been observed.

## § 6. CONCLUSIONS

It is evident from the preceding list of excitation levels in the light nuclei that the data available, upon which to base speculation as to the structure of the nuclei, are very meagre. A knowledge of more than one of the levels in a given nucleus would be especially useful, but so far only one or two instances of this are known from direct measurement of  $\gamma$ -rays. The best of these is the case of  $B^{11}$ , which has levels at 2 and 4 m.e.V. It is probable that most of the levels known from the emission of  $\gamma$ -rays are the first levels above the ground state—the higher levels, providing they exist, requiring rather more energy for their excitation than is available in the usual transformations. Some information regarding levels which are not accessible by direct measurement of  $\gamma$ -rays might be obtained from the known phenomenon of resonance penetration of  $\alpha$ -particles into nuclei, although we have not included data from this source in the preceding list of  $\gamma$ -ray levels. Another method of discovering levels in nuclei might be by means of scattering, although so far this has been found difficult experimentally. If, for instance, an  $\alpha$ -particle colliding with a nucleus has the right amount of energy to satisfy a quantized level in the temporary combination of particles, there should appear, just at this energy, a singularity in the scattering.

A comprehensive knowledge of the energy levels in the nuclei should throw much light upon the question as to how far the identity of the  $\alpha$ -particle and other constituent particles are preserved inside the nucleus, and as to how far the previous structure of a nucleus is preserved throughout a transformation. Con-

cerning the existence of  $\alpha$ -particles in the nuclei, we should search for the 12 m.e.V., or slightly modified 12 m.e.V., level in nuclei which supposedly contain  $\alpha$ -particles. As to the preservation of some of the features of the previous structure of a nucleus throughout a subsequent transformation, it is interesting to note that the radioactive substance obtained by bombarding boron with  $\alpha$ -particles is not identical with that obtained by bombarding carbon with deutons, even though the intermediate aggregate of particles and energy content is presumably the same in the two cases. The difference manifests itself in the half-lives, which are 14 min. in the first case and 10 min. in the second case. A further suggestion of this type of behaviour is furnished by the proton groups resulting from boron bombarded with  $\alpha$ -particles and carbon bombarded with deutons, where the products in both cases are supposedly  $C^{13}$  and  $H^1$ . In the first instance a  $\gamma$ -ray of 3 m.e.V. energy and two groups of protons differing in energy by this amount are found. In the second example the same  $\gamma$ -ray is observed, but only the group of protons which are emitted together with the  $\gamma$ -ray is found. This seems to indicate that in the second mode-of formation of  $C^{13}$  the  $\gamma$ -ray is much more frequently emitted than in the first mode of formation.

## REFERENCES

- (1) W. BOTHE and H. BECKER. *Z. f. Phys.* **66**, 289 (1930).
- (2) W. BOTHE and H. BECKER. *Z. f. Phys.* **76**, 421 (1932).
- (3) J. CHADWICK. *Proc. R.S. A*, **136**, 692 (1932).
- (4) I. CURIE and F. JOLIOT. *Comptes Rendus*, **139**, 1412 (1933).
- (5) H. C. WEBSTER. *Proc. R.S. A*, **136**, 432 (1932).
- (6) J. D. COCKCROFT and E. T. S. WALTON. *Proc. R.S. A*, **129**, 477 (1930).
- (7) G. N. LEWIS, M. S. LIVINGSTON and E. O. LAWRENCE. *Phys. Rev.* **44**, 55 (1933).
- (8) H. R. CRANE, C. C. LAURITSEN and A. SOLTAN. *Phys. Rev.* **44**, 514 (1933).
- (9) H. R. CRANE, C. C. LAURITSEN and A. SOLTAN. *Phys. Rev.* **45**, 507 (1934).
- (10) H. R. CRANE and C. C. LAURITSEN. *Phys. Rev.* **45**, 226 (1934).
- (11) C. C. LAURITSEN and H. R. CRANE. *Phys. Rev.* **45**, 63 (1934).
- (12) C. C. LAURITSEN and H. R. CRANE. *Phys. Rev.* **45**, 493 (1934).
- (13) C. C. LAURITSEN and H. R. CRANE. *Phys. Rev.* **45**, 345 (1934).
- (14) H. BETHE and W. HEITLER. *Proc. R.S. A*, **146**, 83 (1934).
- (15) E. McMILLAN. Am. Phys. Soc. Meeting, Berkeley, June 1934.
- (16) C. C. LAURITSEN. Am. Phys. Soc. Meeting, Berkeley, June 1934.
- (17) H. R. CRANE, L. A. DELSASSO, W. A. FOWLER and C. C. LAURITSEN. *Phys. Rev.* **46**, 531 (1934).
- (18) J. CHADWICK, P. M. S. BLACKETT and G. P. S. OCCHIALINI. *Proc. R.S. A*, **144**, 235 (1934).
- (19) M. L. E. OLIPHANT, B. B. KINSEY and LORD RUTHERFORD. *Proc. R.S. A*, **141**, 722 (1933).
- (20) F. KIRCHNER and H. NEUERT. *Phys. Z.* **35**, 292 (1934).
- (21) I. CURIE and F. JOLIOT. *J. d. Phys. et le Rad.* **4**, 278 (1933).
- (22) J. D. COCKCROFT and E. T. S. WALTON. *Proc. R.S. A*, **144**, 704 (1934).
- (23) H. R. CRANE, L. A. DELSASSO, W. A. FOWLER and C. C. LAURITSEN. Unpublished.
- (24) E. O. LAWRENCE, M. S. LIVINGSTON and G. N. LEWIS. *Phys. Rev.* **44**, 56 (1934).
- (25) M. C. HENDERSON, M. S. LIVINGSTON and E. O. LAWRENCE. *Phys. Rev.* **46**, 38 (1934).

# TRANSFORMATION EFFECTS PRODUCED IN LITHIUM, HEAVY HYDROGEN AND BERYLLIUM, BY BOMBARDMENT WITH HYDROGEN IONS

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*ABSTRACT.* The methods available for producing streams of fast protons and other charged particles are reviewed, as also the methods used for detecting and counting the particles resulting from the transformations effected by them.

A number of specific reactions are then dealt with in detail.

(1)  $\text{Li}^7$  bombarded with protons of sufficient energy gives a pair of  $\alpha$ -particles of range 8.3 cm., emitted practically in opposite directions along the same straight line. The variation in the number of  $\alpha$ -particles with the energy of the incident protons is plotted.

(2)  $\text{Li}^6$  bombarded with protons gives an ordinary  $\alpha$ -particle, together with an atom of the helium isotope of mass 3 (the mass deduced from this and from reaction (5) is 3.0163). It has been reported that  $\gamma$ -radiation is emitted during these transformations, but there is some doubt about the matter.

(3)  $\text{Li}^6$  bombarded with deutons gives a pair of  $\alpha$ -particles of range 12.6 cm. In an alternative mode of reaction, a proton of range 40 cm. is emitted, the residual product presumably being an atom of  $\text{Li}^7$ .

(4)  $\text{Li}^7$  bombarded with deutons gives  $\alpha$ -particles of all ranges up to about 7.8 cm., together with neutrons.

(5) Heavy hydrogen bombarded with deutons. This reaction leads to the emission of protons of range 14 cm., together with singly charged particles of range 1.6 cm. It is probable that the latter are atoms of the hydrogen isotope of mass 3 (or 3.0151 as deduced from this reaction). It is of interest to note that this reaction has a higher probability than any other yet investigated.

As an alternative, the two atoms of heavy hydrogen sometimes react to give the helium isotope of mass 3 together with a neutron.

(6)  $\text{Be}^9$  bombarded with protons. Here the results are not yet satisfactorily accounted for. If it breaks up into  $\text{Li}^6$  and an  $\alpha$ -particle, the latter should have a range 2.3 cm. It is doubtful whether this has been identified or not. Particles with a single positive charge and range 8 mm. are certainly emitted, but it is not clear whether they are protons of different energy from the incident ones, or whether they are deutons; neither is it certain what is the residual nucleus.

(7)  $\text{Be}^9$  bombarded with deutons yields pairs of doubly charged particles of ranges 3 and 1 cm., perhaps nuclei of the helium isotope of mass 5 and that of lithium of mass 6. There are also three or more ranges of protons, as well as neutrons. The latter may arise in the production of the boron isotope of mass 10.

## § 1. THE TECHNIQUE OF ATOMIC TRANSFORMATIONS BY ACCELERATED POSITIVE IONS

THE theory of nuclear structure worked out by Gamow suggested the possibility that protons of moderate energy might be able to penetrate inside a nucleus and produce a change in its structure, and the original experiments of Cockcroft and Walton\* brilliantly verified this hypothesis. Since that time a number of methods for producing fast protons and other ions have been developed, and the methods of detection of the products of the nuclear transformations have been greatly improved. A full account of the methods available up to 1933 is contained in the report of Dr J. D. Cockcroft to the Solvay Conference. We shall mention briefly the more important of these and proceed at once to a discussion of the experimental results.

A beam of positive ions may be produced in a number of ways, but the simplest method of all is by using a discharge through a gas at low pressure, in which the cathode is perforated and so shaped as to concentrate the ions upon the hole. The limiting factor in determining the concentration of ion current in a beam is the mutual repulsion of the particles themselves, and it can easily be shown that in the ideal case of plane parallel electrodes with a potential gradient of  $10^5$  volts/cm. a proton current is limited to about 10 milliamperes per  $\text{cm}^2$ . In practice this current density is rarely approached, as the accelerating fields are only applied over a relatively short portion of the ion-path in the apparatus. This factor may be partially compensated by the focussing action of specially shaped accelerating fields.

It is found in practice that an initial concentrated beam of ions is produced most easily by a properly designed discharge tube, notwithstanding that it requires a relatively high potential and thus bulky auxiliary apparatus. Methods such as the low voltage arc, which require hot filaments of short life and very pure gases for their operation, do not prove so convenient, as the source of ions is not in general easily removed for inspection. Lawrence† uses a hot filament as a source of electron: to ionize the gas, but in his case the ions are produced inside the accelerating space itself.

The beam of ions may be accelerated directly by application of a high voltage in one or more steps. This voltage may be produced by transformers‡, or by a multiplying system of transformer, rectifiers and condensers§, or it may be produced directly electrostatically as in the conveyor-belt method of Van der Graaff||. Where steady sources are not required, as for expansion chamber work, the impulse-generator provides a source of high power and high potential for a short period of time¶. A variation of this method, whereby the ions are accelerated continuously by the field of a steep-fronted potential pulse of relatively low voltage, has been developed by Beams and Snoddy\*\*.

\* *Proc. R.S. A*, 137, 229 (1932).

† Lauritsen, etc., *Phys. Rev.* 46, 514 (1933).

§ Cockcroft and Walton, *Proc. R.S. A*, 136, 619 (1932).

¶ Brasch and Lange, *Z. f. Phys.* 70, 10 (1931).

‡ *Phys. Rev.* 42, 150 (1932).

|| *Phys. Rev.* 43, 149 (1933).

\*\* *Phys. Rev.* 44, 784 (1933).



The problem of applying the potential to a vacuum tube in order to accelerate the ions, resolves itself into providing adequate pumping facilities to remove the gas from the discharge tube and that released by bombardment of the electrodes. The electrodes must be so shaped and disposed that the field over the cathode never exceeds that required to extract electrons from the cold metal, i.e. is kept below about  $10^5$  V./cm. At the same time the action of the fields must be such as to concentrate and not spread the beam of ions.

If ions other than protons are to be used it is essential to provide some means of selecting a given kind of ion. For instance, absolutely pure samples of heavy hydrogen are not in general available, and in order to work with  $H^2$  ions the protons must be eliminated.

Lawrence has devised methods for accelerating ions without application of high voltages, by a series of successive accelerations by the same alternating potential, the ions moving in the field-free space inside the electrodes during the reversed half of the cycle. Such methods require high frequencies and very long apparatus if the electrodes are disposed in a straight line. A charged particle moves in a given magnetic field so that the radius of curvature of the path is proportional to the velocity, that is the time required to perform a complete revolution about the lines of force is constant. Lawrence\* has used this fact to reduce the length of the apparatus required, for it is obvious that if the ions are accelerated by a properly adjusted alternating electric field across a boundary which divides the path into two half-circles, it can be arranged that they arrive always in phase with the electric field, and they will continue to be accelerated and will move in circles of larger and larger curvature. Lawrence has found it possible to make the ions travel round several hundreds of times, and has obtained currents of the order of  $10^{-8}$  amperes at  $3 \times 10^6$  V. However, the magnet required is very large and costly, and considerable technical skill is required for the initial adjustment and subsequent operation of the apparatus.

The methods used for counting the  $\alpha$ -particles, protons and neutrons which appear in the various transformations, are those which have been developed for radioactive work by Wynn-Williams and others, while the presence of  $\gamma$ -rays has been sought by using ionization chambers or Geiger counters. Considerable difficulty is experienced in shielding the detecting apparatus from the disturbing effects of the electric fields and the X-radiation generated in the apparatus. In particular the impact of positive ions, and especially of protons, upon elements heavier than iron, produces an abundance of soft radiation which is very troublesome. Scattered ions from the main beam must be prevented from entering the counting chamber, so that at very high voltages it is impossible to detect many of the more interesting transformations which lead to the production of particles of short range. It is as yet uncertain, in any particular case, how much of the bombarding energy will appear in the products of the reaction, so that accurate values for the energy evolved can only be obtained at low accelerating potentials, where the bombarding energy is negligible in comparison with the total energy.

\* *Loc. cit.*

In order to decide unambiguously the nature of any reaction, it is almost essential to obtain photographs of the tracks of the various particles in an expansion chamber. Special methods have to be employed in this case, and these have been worked out by Dee and by Kirchner. The former has succeeded in passing the beam of bombarding ions into the expansion chamber itself in order to photograph very short-range particles.

It must be realized that whereas in the case of particles from radioactive substances the distribution in time is determined entirely by the laws of probability, it is quite otherwise in the case of the artificial transformations we are considering. Changes in the surface of the targets produced by the intense bombardment, and variations in the accelerating potential and in the intensity of the beam of ions, produce fluctuations which are often many times as great as the probability laws would imply. For this reason it is often necessary to count many more particles than in the radioactive case in order to ensure a given accuracy.

## § 2. THE EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

### (1) *General Remarks*

The phenomena observed are the emission of particles and of radiation from the bombarded elements. These particles can only be observed if their energy is such that they are able to penetrate through the window system used and enter the detecting apparatus. In the case of the experiments carried out in Cambridge the thinnest windows have corresponded to about 2.5 mm. of air, and particles with a range greater than about 6 mm. are detected with certainty. Measurements are made of the energies of the particles by observation of their ranges in air or in mica, in combination with the known energy-range relations. For  $\alpha$ -particles with ranges from 3 to 12 cm. this relation is very well known, but in some other cases it is subject to considerable doubt, so the observed ranges and the energy of the bombarding particles will be given in addition to the probable energies in discussing the results. The nature of the particles, i.e. whether  $\alpha$ -particles or protons or otherwise, is obtained from the form of the absorption curve and the magnitude of the ionization produced by the passage of a particle through the detecting chamber.

Interpretation of any one observation involves an application of momentum considerations to the particles observed, and in addition of a generalized form of the conservation of energy which admits the equivalence of mass and energy according to the relation of the relativity theory

$$E = mc^2,$$

or where energy is expressed in electron-volts, and mass in terms of the standard mass-unit which is  $\frac{1}{16}$  of the mass of the  $\text{O}^{16}$  isotope of oxygen

$$E = m \cdot 933 \cdot 10^6 \text{ e.V.}$$

It is necessary that the masses of the particles concerned be known as accurately

as possible. The masses used in what follows, and for which experimental values are available, are\*:

$$H^1 = 1.00778 \pm 0.00005,$$

$$H^2 = 2.01363 \pm 0.00007,$$

$$He^4 = 4.00216 \pm 0.00013,$$

$$Li^6 = 6.0145 \pm 0.0003,$$

$$Li^7 = 7.0146 \pm 0.0006,$$

$$Be^9 = 9.0155 \pm 0.0006,$$

$$B^{10} = 10.0135 \pm 0.0005.$$

The mass of the neutron is taken as  $1.0080 \pm 0.0005$ , which is the latest value given by Chadwick and Goldhaber†. It is probable that the mass is much closer to 1.0080 than the limits given by Chadwick.

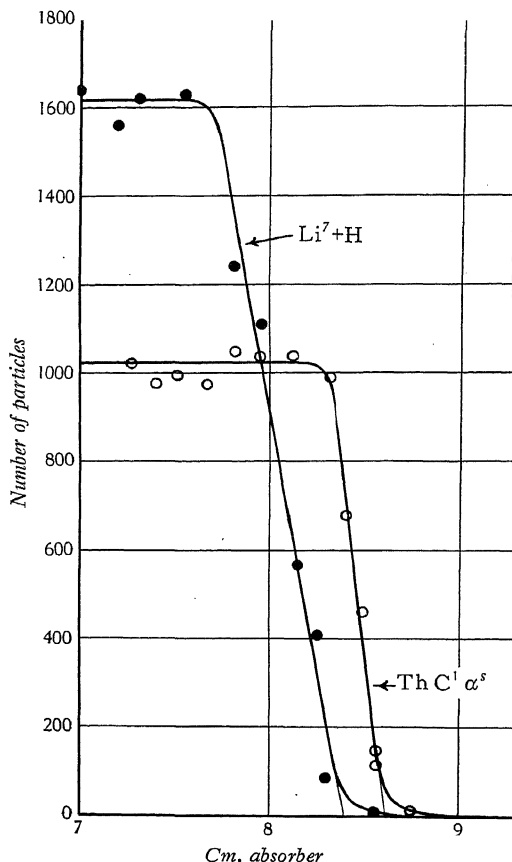


Figure 1.

In what follows the nature of the phenomena which have been observed, and the probable nuclear reactions involved, will be discussed without reference to the

\* See Aston, *Isotopes*, 1933 edition, and later papers by Bainbridge in *Phys. Rev.*

† *Nature*, 134, 237 (1934).

actual mechanism of capture of the bombarding particle or of the emission of the products of the transformation. In the case of lithium the reactions peculiar to the isotopes  $\text{Li}^6$  and  $\text{Li}^7$  are identified with certainty from the experiments on the separated isotopes described by Oliphant, Shire and Crowther\*.

(2)  $\text{Li}^7 + \text{H}^1$

This is the nuclear transformation first investigated by Cockcroft and Walton in their pioneer experiments†. When lithium is bombarded by protons at accelerating potentials greater than about 20,000 V.,  $\alpha$ -particles are emitted in large

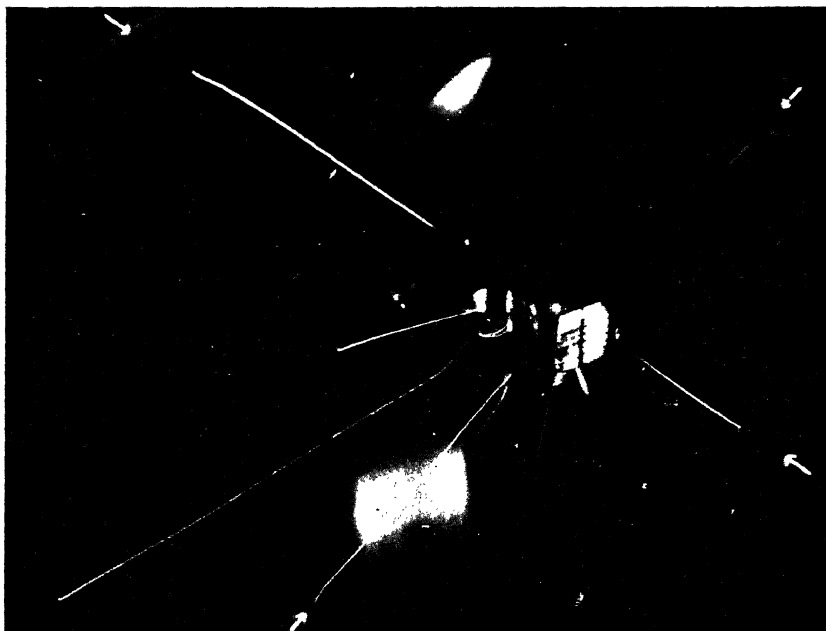
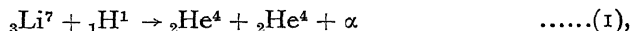


Figure 2. The arrows indicate two opposite pairs of particles. The tracks on the right have traversed the target and its support and are therefore shorter than those on the left.

numbers. It is found that these particles constitute a single homogeneous group of mean range  $8.31 \pm 0.03$  cm. at 187,000 V., and in order to account for their production Cockcroft and Walton assumed the transformation



where  $\alpha$  is the total energy of the resultant  $\alpha$ -particles for zero bombarding energy, and is equal to  $17.04 \pm 0.06 \times 10^6$  e.V. The mass of  $\text{Li}^7$  calculated from this reaction is then  $7.0147 \pm 0.00016$ , in excellent agreement with the mass found by Bainbridge. Figure 1 shows a typical absorption curve for these  $\alpha$ -particles and

indicates the method employed, viz. that of comparing the range directly with 8.6 cm.  $\alpha$ -particles from ThC' under identical conditions.

Momentum considerations require that the two  $\alpha$ -particles in (1) should be emitted in opposite directions except for a small correction due to the momentum of the bombarding proton, and expansion chamber photographs such as that reproduced in figure 2, obtained by Dee and Walton\* and by Kirchner†, show at once that this is so.

The variation of the number of  $\alpha$ -particles in the 8.4 cm. group with the energy of the incident protons has been investigated over different parts of the energy range by Cockcroft and Walton‡, Oliphant and Rutherford§, and Henderson||, and

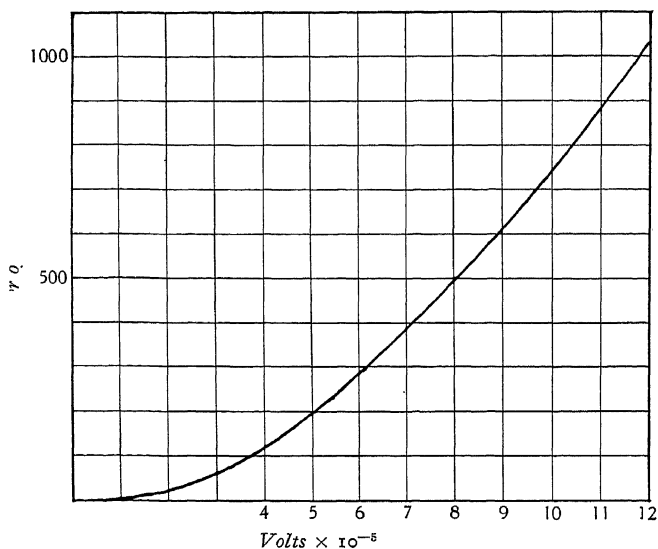


Figure 3.

a curve compounded of all these results is given in figure 3. For energies below about 100,000 V. the curve is very closely exponential, but at high energies it approaches a straight line. Henderson has pointed out that this is consistent with approach towards a constant probability of transformation in nuclear collisions which take place with energy above about 200,000 V., the number of  $\alpha$ -particles increasing at high energies proportionally with the number of nuclear collisions, i.e. with the range of the bombarding particle in the target material. The absolute efficiency, i.e. the number of protons completely absorbed in a pure lithium target which are required to produce a pair of  $\alpha$ -particles, is of the order of  $10^8$  at 400,000 V.¶ It has been shown that a layer of lithium much less than one atom in average thickness will give a large number of  $\alpha$ -particles, and the presence of very small con-

\* *Proc. R.S. A*, **141**, 733 (1934).

† *Loc. cit.*

‡ *Phys. Rev.* **43**, 98 (1933).

§ *Naturwiss.* **21**, 473 (1933).

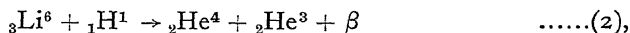
¶ *Proc. R.S. A*, **141**, 259 (1933).

¶ Cockcroft and Walton, *loc. cit.*

taminations of such an active element on other targets which are being investigated can give rise to effects large enough to mask completely any transformation of the targets themselves.

### (3) $\text{Li}^6 + \text{H}^1$

Walton and Cockcroft\* observed the presence of short-range  $\alpha$ -particles emitted from lithium bombarded by protons. These were investigated in detail by Oliphant, Kinsey and Rutherford† who showed that they consisted of two groups of 11.5 mm. and 6 to 8 mm. range respectively, and suggested that they might arise from the reaction



where  $\beta$  is  $3.6 \pm 0.1 \times 10^6$  e.V. Momentum considerations lead to the conclusion that the particles are emitted in pairs opposite one another, the  $\text{He}^4$  particles



Figure 4. The white ball in the centre is due to scattered protons from the primary beam. The tracks appear blurred because of this diffuse ionization.

constituting the shorter range and the new isotope of helium of mass 3 the longer range. Dee‡ has photographed these particles by passing the beam of protons into the chamber itself, where it struck a thin target of lithium, and he has shown that the particles are indeed emitted in opposite pairs (figure 4). (Kirchner§, on the basis of range measurements made in the Wilson chamber, has reported the presence of a third still shorter range, but these observations do not seem to fit in very well with any reactions which can be written down, and we have so far failed to detect the third short range by electrical counting methods.) The mass of  $\text{He}^3$  calculated from the known masses and the observed energies in equation (2) is  $3.0163 \pm 0.0004$ . We shall see that this mass is in good agreement with that deduced from a further transformation which also gives rise to  $\text{He}^3$

\* *Nature*, **131**, 23 (1933).

† *Nature*, **132**, 819 (1934).

‡ *Proc. R.S. A*, **141**, 722 (1933).

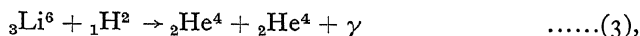
§ *Phys. Z.* **35**, 292 (1934).

The variation in the number of short-range particles with the energy of the bombarding protons is identical, within the limits of error, with the variation in the number of 8.4 cm.  $\alpha$ -particles. The efficiency of the production of short-range particles in a target of pure  $\text{Li}^6$  is about 30 times that of 8.4 cm. particles in a target of pure Li?

Lauritsen and Crane\* have reported the existence of  $\gamma$ -rays of about  $1.5 \times 10^6$  e.V. energy when Li is bombarded with protons. It is difficult to see how this can arise. Trautenberg has also investigated this question, and Oliphant and Westcott† searched carefully for such  $\gamma$ -rays with a Geiger counter shielded with just sufficient lead to exclude X-rays from the apparatus, and placed a few centimetres from the target. They detected no  $\gamma$ -rays although the method could have detected them if present to the extent of 0.5 per cent of the 8.4 cm. particles produced; the few impulses which were observed could be ascribed to neutrons produced by the secondary reaction of the  $\alpha$ -particles with the lithium.

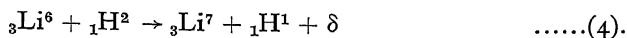
#### (4) $\text{Li}^6 + \text{H}^2$

The emission of  $\alpha$ -particles in this reaction was first observed by Lawrence‡ and was investigated in detail by Oliphant, Kinsey and Rutherford§ and by Dee and Walton§. The transformation involved is probably



where the  $\alpha$ -particles are emitted in pairs opposite one another with an extrapolated range of  $12.60 \pm 0.05$  cm.||, and  $\gamma$  is therefore  $22.08 \pm 0.12 \times 10^6$  e.V. Figure 5 is a reproduction of a photograph of this reaction taken in an expansion chamber by Dee and Walton. The mass of  $\text{Li}^6$  calculated from equation (3) is  $6.0143 \pm 0.00019$ , in good agreement with that given by Bainbridge.

The emission of protons of range about 30 cm. as a result of bombarding Li with  $\text{H}^2$  at 500,000 V. was observed by Walton and Cockcroft¶. Lawrence\*\* had reported a range of about 40 cm. at higher bombarding energies. It appears that the neutron from the  $\text{H}^2$  nucleus is captured by the  $\text{Li}^6$  with emission of the proton to give the heavier  $\text{Li}^7$  nucleus



The observed value of  $\delta$  is  $4.8 \pm 0.2 \times 10^6$  e.V., whereas the value calculated from the measured masses is  $5.3 \pm 0.7 \times 10^6$  e.V., and that given by the masses obtained from equations (1) and (3) is  $5.16 \pm 0.20 \times 10^6$  e.V. The agreement is just within the limits of error but is scarcely as satisfactory as might be expected. It is possible that the discrepancy may arise from uncertainties in the range-velocity relation for protons, especially as the range is measured in mica.

\* *Phys. Rev.* **44** (1933). See also their report to this Conference, in which the existence of hard  $\gamma$ -rays is clearly indicated.

† Unpublished.

‡ *Phys. Rev.* **44**, 55 (1933).

§ *Loc. cit.*

¶ The greater part of the difference between this value and that given previously (13.2 cm.) is to be ascribed to variations in the stopping power of mica with velocity of the  $\alpha$ -particles.

¶ *Proc. R.S. A*, **144**, 704 (1934).

\*\* *Phys. Rev.* **44**, 55 (1933).

(5)  $\text{Li}^7 + \text{H}^2$ 

It was shown by Oliphant, Kinsey and Rutherford\* that the bombardment of  $\text{Li}^7$  by heavy hydrogen produced an emission of  $\alpha$ -particles with all ranges up to about 7.8 cm. An absorption curve obtained more recently in air, and compared directly with the known radioactive range of 8.62 cm. from  $\text{ThC}'$ , is given in figure 6. The form of the end of the range was established by using a target of  $\text{Li}^7$  free from  $\text{Li}^6$  in a separate experiment, and the two curves were fitted at 6.0 cm.

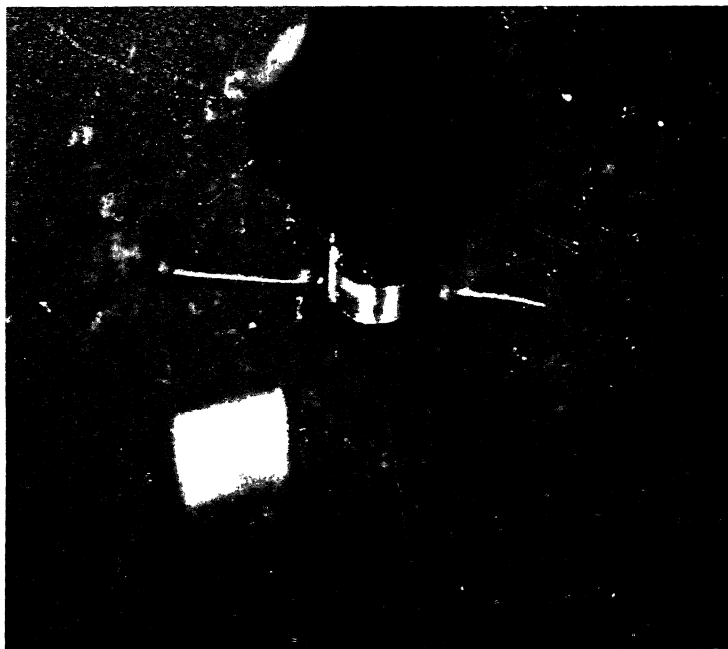


Figure 5. An opposite pair of 12.6 cm. particles. The fainter track in the foreground is probably a proton from reaction (4).

It is seen that over the greater part of its length the number-range relation is very accurately linear, a peculiarity which is borne out by the differential curve shown in the figure and obtained by counting only those deflections of the oscillograph greater than 1 cm. The end of the range tails out to between 7.6 and 7.8 cm. More careful experiments with thicker targets of  $\text{Li}^7$  will be necessary to determine the end of the range with precision.

Owing to the penetration of the bombarding particles into the target, and the roughness of the oxidized surface of the metal, the  $\alpha$ -particles emitted suffer very appreciable "straggling." This is most easily seen in the case of a pure range such as the 8.4 cm. particles in figure 1, where the "straight" dropping portion of the

\* *Loc. cit.*



curve extends over about 6 mm., as compared with less than 2 mm. for the particles from a clean source of ThC'. It is evident that particles which, in the absence of straggling, would all possess the same range, begin to fail to be counted some 6 mm. from the real end of the extrapolated range. In the case of a distributed

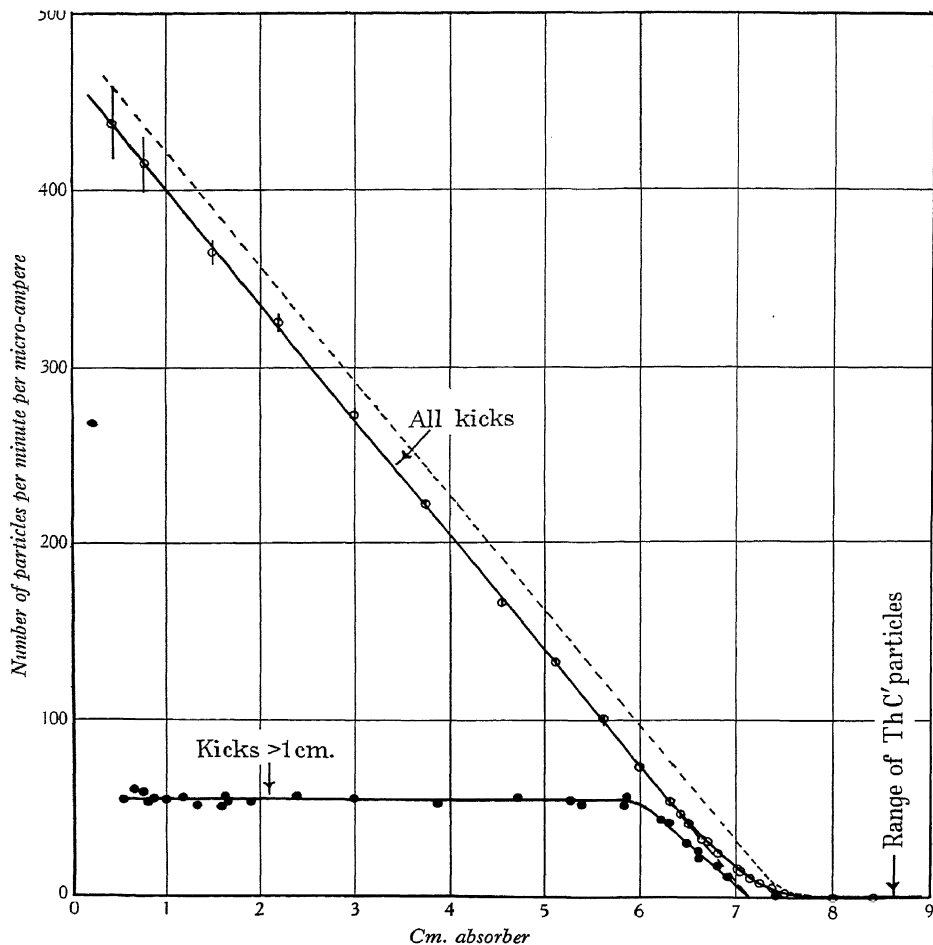
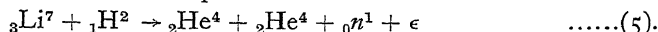


Figure 6.

group of particles, as in figure 6, it is then clear that the real range-number curve will lie to the right of the observed curve except at the end, where the two must coalesce. If all the particles failed to be counted 6 mm. from the end of the range the curve would be displaced 6 mm. to the right. But it is evident that as the "straggling" is roughly linear the real curve will in fact be displaced about half the distance. A curve corrected in this way is dotted in the figure.

The bombardment of  $\text{Li}^7$  by  $\text{H}^2$  ions gives rise to a copious emission of neutrons\*. Observation of the magnitude of the ionization produced by the recoil nuclei in pure helium leads to the conclusion that the neutrons are present with energies at least as high as  $6 \times 10^6$  e.V. (cf. figure 9), but the actual maximum energy and the distribution of energy among them have not yet been determined. The effective cross-section of lead nuclei for these neutrons is found to be very close to that found by Chadwick for the neutrons from beryllium bombarded by  $\alpha$ -particles from polonium. Bjerger and Westcott† have shown that neutrons from  $\text{Li}^7 + \text{H}^2$  produce in light elements the same radioactive effects as those observed by Fermi for neutrons from beryllium bombarded by  $\alpha$ -particles from radon in equilibrium with its products. It seems probable, therefore, that the neutrons produced in the present reaction are identical with those observed by Chadwick.

We assume that the neutrons and  $\alpha$ -particles are due to the same reaction



The distribution of energy among the particles will then be determined by unknown conditions immediately preceding the disruption, and it is possible to satisfy the conservation of energy and momentum in an infinite number of ways. An  $\alpha$ -particle with the greatest possible energy, i.e. corresponding with the end part of the tail of the absorption curve of figure 6, should arise from the escape of one  $\alpha$ -particle opposite an  $\alpha$ -particle and neutron which escape together parallel to one another (figure 7). However, the absorption curve suggests that this is a rare



Figure 7.

event, and indeed it may never be possible, owing to mutual forces, for the neutron and  $\alpha$ -particle to move together with the same energy as if there were no forces between them. As we know nothing of the limitations set by such considerations, and we cannot infer the actual angular distribution of the particles from the absorption curve, we are unable to calculate  $\epsilon$  unambiguously. If we assume that the  $\alpha$ -particles of maximum energy correspond approximately with the condition of figure 7, i.e. possess nearly  $\frac{5}{11}$  of the total energy  $\epsilon$ , we find

$$\epsilon \geq 14.60 \pm 0.25 \times 10^6 \text{ e.V.}$$

The value calculated from the known masses in equation (5) is

$$\epsilon = 14.9 \pm 0.8 \times 10^6 \text{ e.V.}$$

The agreement is exceedingly satisfactory. The actual distribution of angle between the particles can only be determined by observations in a Wilson chamber.

## (6) $\text{H}^2 + \text{H}^2$

(a) Lawrence‡ and Cockcroft and Walton§ observed that there was an emission of protons of about 14 cm. range from all substances bombarded by heavy hydrogen ions, and the former suggested that the  $\text{H}^2$  nucleus was unstable and broke up on

\* Crane, Lauritsen and Soltan, *Phys. Rev.* **44**, 692 (1933).

† *Nature*, **134**, 177 (1934).

‡ *Phys. Rev.* **44**, 56 (1933).

§ *Proc. R.S. A*, **144**, 704 (1934).

impact with other nuclei. On the other hand, experiments made by Rutherford and Kempton\* and by us showed that bombardment of  $H^2$  with  $\alpha$ -particles or with protons produced no detectable disintegration. However, it was shown by Oliphant, Harteck and Rutherford† that the bombardment of  $H^2$  with  $H^2$  led to the emission of an enormous number of 14 cm. protons, and that these were accompanied by a second group of an equal number of singly-charged particles of range about 1.6 cm. This suggested that the particles were emitted in pairs, a long-range and a short-range particle opposite one another. Photographs in the expansion chamber obtained by Dee‡ fully substantiated this suggestion. A beautiful example of such a pair is reproduced in figure 8.

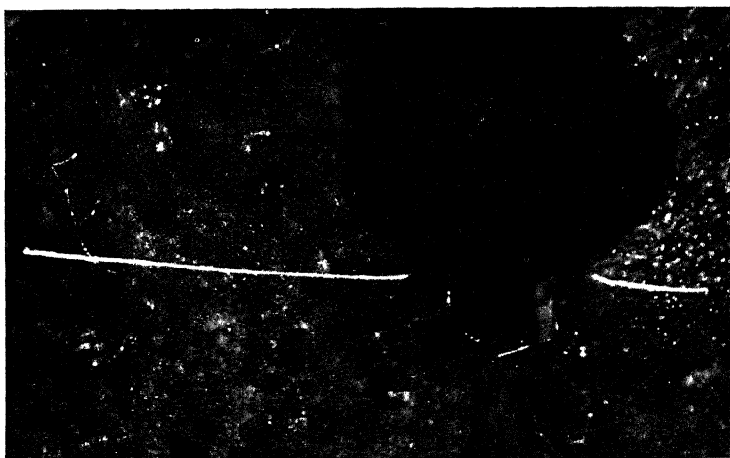
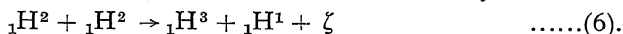


Figure 8. A 14 cm. proton opposite an  $H^3$  particle of about 1.6 cm. range.

Momentum considerations require that the particles shall have different masses, and it is found that the assumption that the 14 cm. group consists of protons and the 1.6 cm. group of particles of mass 3 satisfies the conditions fairly well:



The range of the proton as determined in mica is  $14.3 \pm 0.3$  cm., and using Duncanson's§ calculated range-energy relation this corresponds to an energy of  $3.0 \pm 0.1 \times 10^8$  e.V. The proton receives  $\frac{3}{4}$  of the total energy so that  $\zeta$  is  $4.0 \pm 0.1 \times 10^8$  e.V. The mass of  $H^3$ , a new, still heavier isotope of hydrogen of mass 3, is then  $3.0151 \pm 0.0001$ . The range of the  $H^3$  particle can be calculated from the known laws and comes out to be 1.74 cm., in fair agreement with the observed range of 1.6 cm. Bleakeney and Harnwell|| have actually detected the presence of this new hydrogen in samples of  $H^2$  which had been subjected to an intense electrical discharge at about 70,000 V.

\* *Proc. R.S. A*, **143**, 724 (1934).

† *Nature*, **133**, 564 (1934).

|| *Phys. Rev.* **45**, 655 (1934).

† *Proc. R.S. A*, **144**, 692 (1934).

§ *Proc. Camb. Phil. Soc.* **30**, 102 (1934).

The reaction (6) can be observed at very low bombarding potentials, and we have detected particles at 20,000 V. In a collision between particles of equal mass only half the bombarding energy is available for mutual reaction, so that the transformation under consideration possesses a probability far greater at any given low energy than any other known reaction. At 100,000 V. the absolute yield of protons is about 1 in  $10^6$  if the bombarding particles are completely absorbed in heavy hydrogen. It is evident that this group of protons will always be present

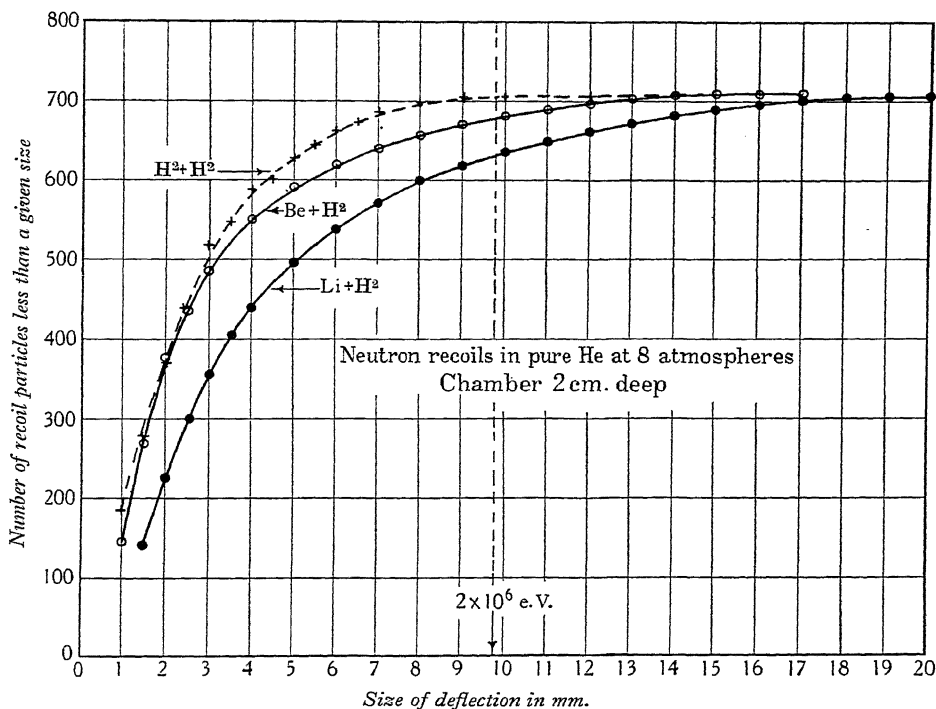
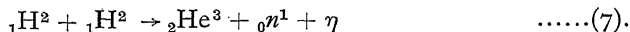


Figure 9.

when targets are bombarded by H<sup>2</sup> owing to the deposition of heavy hydrogen on and in the target from the beam itself.

(b) Bombardment of H<sup>2</sup> with H<sup>2</sup> is found to yield large numbers of neutrons\* in addition to charged particles. Rough estimates of the number showed that this was nearly the same as the number of 14 cm. particles. Using a bombarding potential of 20,000 V. it is easy to obtain more than 1000 recoil particles per minute in a helium-filled counting chamber placed a few cm. from the target. The radius of cross-section of lead nuclei for removing neutrons from the chamber was found to be  $7.8 \times 10^{-13}$  cm., in good agreement with Chadwick's value of  $7 \times 10^{-13}$  cm.

for the neutrons from beryllium bombarded by polonium  $\alpha$ -particles. It seems probable that the transformation which produces the neutrons is



The energy  $\eta$  can be estimated in two different ways. The energy of the neutrons has been measured by observation of the size of the oscillograph deflections produced by the recoil nuclei in a counting chamber filled with helium at 8 atmospheres pressure. In figure 9 the number of deflections smaller than any given size is plotted against that size. The relation between size of deflection and energy of the recoil nuclei was known from observation of the deflections produced by polonium  $\alpha$ -particles at different parts of the range, and it is seen that the maximum energy



Figure 10.  $\text{H}^1$  and  $\text{T}^3$  particles. The isolated track in the foreground is that of a neutron recoil particle.

of the neutrons from  $\text{H}^2$  on  $\text{H}^2$  is very nearly  $2 \times 10^6$  e.v. The curves obtained in the same apparatus for  $\text{Be} + \text{H}^2$  and  $\text{Li} + \text{H}^2$  are plotted for comparison, and it is evident that the energy in these cases is considerably greater than  $2 \times 10^6$  e.v. Bjerger and Westcott\* have observed that neutrons from  $\text{H}^2 + \text{H}^2$  are unable to produce some of the radioactive nuclei found by bombarding light elements with neutrons from other sources, a result which suggests that the energy is low†. Dee has photographed recoil nuclei from these low-energy neutrons in the expansion chamber, and from his knowledge of the direction of incidence of the neutrons, and the energy and direction of the recoil nuclei, he has concluded that the neutrons are probably homogeneous in energy, and that this energy is very close to  $2 \times 10^6$  e.v. In

\* *Nature*, 134, 177 (1934).

† Fermi and his collaborators have now shown that it is probably the very slow neutrons which produce these radioactive effects, and our conclusions must therefore be modified. (Note added Oct. 29th.)

figure 10 a photograph is reproduced showing  $H^1$  and  $H^3$  tracks and one prominent neutron recoil track from the reaction of H with H. We must conclude, therefore, that the energy  $\eta$  is  $2.67 \pm 0.10 \times 10^6$  e.V.

On the other hand the energy may be calculated from the mass of  $He^3$  given by the reaction  $Li^6 + H^1 \rightarrow He^3 + He^4$  (i.e.  $3.0163 \pm 0.0004$ ), together with the other known masses in equation (7), and in this case we find  $\eta = 2.6 \pm 0.6 \times 10^6$  e.V., in good agreement with the value found experimentally.

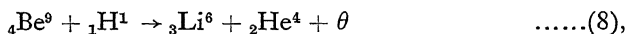
The energy of the  $He^3$  particle in transformation (7) is  $0.67 \times 10^6$  e.V., and the range will therefore lie between 5 and 7 mm. It is difficult to observe a range as short as this, and it has not yet been detected. It is hoped that, by observing in the direction of the bombarding beam, the extra momentum given to the  $He^3$  nucleus will make the range long enough to be detected and measured in the presence of the  $H^3$  particles.

Ladenburg\* has compressed the residual gases from a discharge through  $H^2$  into a Geiger counter, and concluded that the  $He^3$  which Bleakeney† has shown to be present in appreciable quantity is not energetically unstable, as the high mass might suggest.

Klemperer, in some unpublished experiments with the author, has shown by using the coincidence method with two thin-walled Geiger counters that there is no evidence for the production of  $\gamma$ -rays with quantum energy greater than about  $10^6$  e.V. in the reaction of  $H^2$  with  $H^2$ .

#### (7) $Be^9 + H^1$

The mass of  $4Be^9$  is 9.0155 as measured by Bainbridge, and it is therefore greater, by 0.003 units, than the mass of two  $\alpha$ -particles and a neutron. This suggests the possibility that the beryllium nucleus should be energetically unstable, and might break up spontaneously into two  $\alpha$ -particles and a neutron, or into  $He^4 + He^5$ , with an evolution of energy. Careful search for an emission of charged particles from beryllium has yielded no result, so we must conclude that it is a stable structure. However, it might be expected that bombardment with fast protons would lead to the transformation



where  $\theta$  is  $6.2 \times 10^6$  e.V. The  $\alpha$ -particles should have a range of about 2.3 cm. Cockcroft and Walton† and Lawrence‡ have reported an emission of 3 cm. particles from beryllium under proton bombardment, but as the yield was small it is difficult to be quite sure that the range observed was due to beryllium and not to an impurity. We have bombarded solid beryllium with protons at 250,000 V. and found a range of  $\alpha$ -particles of approximately 2.6 cm., but as a fresh iron target gave the same range in equal numbers it is almost certainly not due to beryllium. The particles might possibly arise from carbon or oxygen, or even from boron.

Recently Dee observed a copious emission of particles of about 9 mm. range when a mixture of  $H^1$  and  $H^2$  was used to bombard beryllium at about 500,000 V. We

\* *Phys. Rev.* **46**, 81 (1934).

† *Loc. cit.* p. 149.

‡ *Bull. Amer. Phys. Soc.* **8**, 4, 13 (1933).

investigated this and found that the particles were singly charged, i.e. were hydrogen ions, and that they were due to the protons and not the heavy hydrogen. The reaction is an exceedingly probable one, the number of particles at 200,000 V. being comparable with that observed from the lithium reactions. Figure 11 shows the way in which the number of the particles increases with the accelerating potential. The range is about 7 mm. at 100,000 V., and hence if they are protons they possess an energy of 300–400,000 V. It is difficult to account for the production of this group, as the entry of a proton and subsequent ejection of a more energetic proton without other particles implies that energy is abstracted from the nucleus without other change. There is no detectable emission of neutrons or of

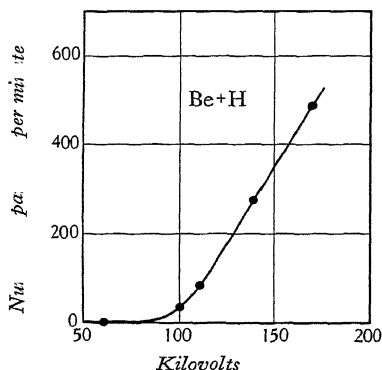
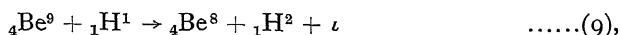


Figure 11.

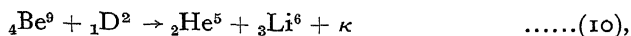
$\gamma$ -rays, and the particles appear to bend in a magnetic field as if they were positively charged. The reaction may be



where the mass of  $\text{Be}^8$  is about 8.009. There is no evidence for the existence of  $\text{Be}^8$ , and for the present we are unable to give any satisfactory explanation for the production of the particles.

#### (9) $\text{Be}^9 + \text{H}^2$

We have observed in this case two groups of doubly-charged particles of ranges 3 cm. and 1 cm. respectively, as shown in figure 12. Careful counting shows that these two groups are present in very nearly equal numbers, a fact which suggests that they are emitted opposite one another. The transformation suggested is



where  $\kappa$  is about  $8.4 \times 10^6$  e.V., and the mass of  $\text{He}^5$  is about 5.006. This would mean that the 1 cm. group is to be ascribed to  $\text{Li}^6$ , and the range seems somewhat too long on general considerations. Dee has obtained some evidence that the particles are emitted in opposite pairs, but the work is as yet incomplete.

In addition to the  $\alpha$ -particles beryllium yields three or more ranges of protons, the most prominent of which occur at about 8, 14 and 26 cm. respectively at 200,000 V. The 8 cm. group may arise, as suggested in the case of other targets\*, from oxygen, as it is always present. The 14 cm. group is probably due to deposited heavy hydrogen, while there is as yet no explanation of the 26 cm. group.

Neutrons are emitted in large numbers from beryllium when bombarded by  $H^2$ †, whilst Kurie‡ reports the presence of neutrons with energies up to  $20 \times 10^6$  e.V. On the other hand our own measurements, as shown in figure 9, suggest that there are

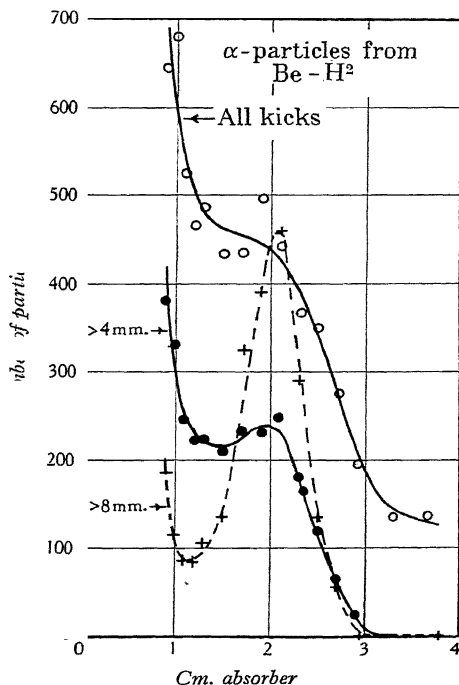
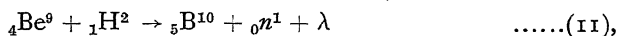


Figure 12.

not many neutrons with energies greater than about  $3 \times 10^6$  e.V., and this is supported by the observations of Bjerger and Westcott§ that, like the  $H^2 + H^2$  neutrons, the neutrons from  $Be + H^2$  will not give rise to some radioactive nuclei created by other sources of neutrons||. The transformation which appears most natural is



but  $\lambda$  is then about  $7 \times 10^6$  e.V. It may be that part of the energy appears as a  $\gamma$ -ray, as suggested by Crane and Lauritsen¶.

\* Cockcroft and Walton, *Proc. R.S. A*, 144, 704 (1934).

† Crane, Lauritsen and Soltan, *Phys. Rev.* 44, 692 (1933).

‡ Privately communicated by Prof. Lawrence.

|| See note, p. 158.

§ *Loc. cit.*

¶ *Phys. Rev.* 45, 226 (1934).



## DISCUSSION

LORD RUTHERFORD. Although I have followed with much interest the work on transmutation from the beginning, I have found it most interesting to listen to the summaries of the present position of this subject by the various speakers. In particular I have been much interested in the evidence obtained by Lauritsen and Crane that high energy  $\gamma$ -rays are emitted in the bombardment of lithium by protons. The nature of the transformations that give rise to this  $\gamma$ -ray is of much interest, and the evidence that they have obtained on the absorption of such high frequency  $\gamma$ -rays is of great value.

When we sum up the present results, it appears that every type of possible reaction occurs in these transformations with greater or less frequency, provided the reactions are consistent with the conservation of energy in the wide sense.

We have already examined a number of reactions in the case of lithium and probably still more will ultimately come to light. As to the future, it seems likely that before long we must extend our experimental methods to study the effect produced by bombarding particles of still higher energy than those now available. In addition, it will be of much interest to study the effect of bombarding elements with more complex nuclei than protons, deuterons, or  $\alpha$ -particles.

At the present time, I think it is of importance to examine very fully the reactions which occur in the transmutations of the lighter elements. When we come to the heavier elements which may consist of a number of isotopes, results will inevitably be more complicated and difficult of interpretation. The essential nature of the process of transformation can probably be more carefully studied in the lighter and simpler elements in the same way that our knowledge of the spectra of the elements arose mainly from a detailed study of the lighter elements.

Dr H. A. BETHE. I should like to point out that the  ${}^3\text{He}$  nucleus should not show radioactivity if the atomic weight is smaller than  $3.0162$  which seems reconcilable with the experiments of Rutherford and Oliphant. For, in the atomic weight of  ${}^3\text{He}$ , two electrons are taken into account, as against only one in  ${}^3\text{H}$ . Therefore,  ${}^3\text{He}$  can only emit positrons, if its atomic weight is greater than that of  ${}^3\text{H}$  together with a positron and negative electron, i.e.  $3.0162^*$ . The  ${}^3\text{He}$  nucleus should, however, not be stable, but capable of transforming into  ${}^3\text{H}$  by absorbing one of its K-electrons and emitting a neutrino. The lifetime of  ${}^3\text{He}$  should be of the order of a few years, and one could perhaps detect spectroscopically that in a tube containing initially pure  ${}^3\text{He}$  the spectrum of  ${}^3\text{H}$  appears after some time.

Dr J. CHADWICK. There are many questions connected with these transmutations which should perhaps be discussed here but I will confine my remarks to one aspect of the  $\alpha$ -particle transmutations. The experimental technique applied to these disintegrations has been developed so far that we can now get very precise information about the interaction of an  $\alpha$ -particle with an atomic nucleus. In our report Dr Feather and I have described how the experiments on the disintegration of

\* Indeed, Lodenburg and his collaborators have found no radioactivity in  ${}^3\text{He}$ .

aluminium have fixed the height of the potential barrier of this nucleus, the positions of several resonance levels, and the positions of some  $\alpha$ -levels relative to the proton level. At the present moment the results with other elements are not so detailed as this, but there is no doubt that we shall soon have a good picture of the potential barriers of a series of atomic nuclei. I hope that by comparing the results we shall get at least a formal representation of the characteristics of the potential barriers; but it seems to me that the problem is now ready for attack from the theoretical side. I do not expect that one will be able to probe very deeply into the structure of nuclei in this way but I feel sure that it will bring us at least one step farther into the nucleus. I should like to commend this problem to the theoretical workers.

Dr L. R. HAFSTOD. I wish to take this opportunity to report that our most recent experiments on the artificial radioactivity produced in a carbon target by proton bombardment have given results in agreement with those of Dr Cockcroft.

In earlier work we had found that the effect produced by deuteron bombardment was at least 8000 times the minimum which we could detect, while the proton effect was not observable. On the basis of this result we suggested that the effects ascribed to protons by other investigators might be caused by a very small amount of deuterium in the bombarding beam.

In our most recent experiments made at about 900 kV., we have increased both the effective current of bombarding particles and the sensitivity of our detecting apparatus. We now find a small but definite effect with a decay period of from 10 to 11 min. which we must ascribe to protons. The ratio of the two effects, however, remains as before, our new measurements giving a deuteron effect between 7000 and 17,000 times greater than the proton effect. The first figure is obtained on the assumption that the mass two beam contains only deuterons, and is therefore conservative. The second figure assumes 50 per cent deuterons which is probably more nearly correct.

Dr W. R. HARTREE. Our attention has been drawn during the Conference to one phenomenon in which there is a disagreement between the results of experiment and the results of calculations based on Dirac's theory of the electron. I wish to draw attention to another such phenomenon, namely the polarization of electron beams as shown by experiments on double scattering, according to the recent experiments of Dymond\*. The disagreement seems to be rather definite in both cases, and raises the important question of the need for a modification in Dirac's equation to account for phenomena in the range of comparatively small energies (small, that is, compared to  $137 mc^2$ ) involved in these experiments, apart from the modifications known to be required for very high energies.

Mr M. GOLDBABER. I should like to mention the probability of artificial nuclear transformations and its connexion with the vector model of the nucleus. We expect that in artificial nuclear transformations where only *heavy* particles (protons, neutrons,

\* *Proc. R.S. A.*, 145, 657 (1934).

$\alpha$ -particles, etc.) and photons are involved, the general principles of quantum mechanics will hold. They lead to the *conservation laws* which have been a guide throughout all work done on artificial nuclear transformations. These laws are:

The conservation of (i) electric charge, (ii) mass-energy (in the relativistic sense), and (iii) momentum.

Lately there have been published some considerations on the conservation of (iv) angular momentum, in artificial nuclear disintegrations\*.

We want here to show that a somewhat more detailed discussion of artificial nuclear transformations is possible if one makes use of the theorem of quantum mechanics that the *spin part* of the angular momentum is *approximately* a constant of motion, provided that the interaction forces depending on the directions of the spins are small compared with the total forces†.

§ 1. We shall assume for the following that a nucleus is built up from protons and neutrons which may be partly combined to form  $\alpha$ -particles (Heisenberg, Iwanenko, Majorana). We take it as a working hypothesis that the "directional" part of the interaction forces is either only magnetic or at least not of higher order of magnitude than the interaction forces between nuclear magnetic moments ( $\sim 1/1000$  Bohr magneton). For small relative velocities ( $(v/c)^2 \ll 1$ ) of the interacting nuclei these forces may then be regarded as small compared with the total interaction forces. We therefore conclude that

(A) a nuclear transformation  $A + B \rightarrow C + D + E + \dots$  is "forbidden" (i.e. improbable) if the spin of a proton or neutron has to change its direction during this process.

We shall further make use of the result of Gamow's theory of artificial disintegration of nuclei that—disregarding cases of resonance—

(B1) those bombarding particles B which have an orbital momentum  $l_1 > 0$  with respect to the bombarded nucleus A have only a small probability of entering into the interior of A, which holds for small "effective" velocities of B ( $\hbar/M_B v_{\text{eff.}} \gg$  radius of A).

And also that

(B2) when the particles *resulting* from the nuclear transformation have small relative velocities, the reaction is not a probable one if they have a mutual angular momentum  $l_2 > 0$ .

As it is not yet possible to find reliable values experimentally for the absolute probabilities of nuclear reactions, we shall consider here only relative probabilities. It is convenient to introduce for general considerations about nuclear reactions a symbol  $\begin{pmatrix} Z \\ M \end{pmatrix}$  for nucleus of charge  $Z$  and mass number  $M$ . We define now a reaction

\* G. Beck, *Handb. d. Radiologie*, 2nd ed. 6, 390 (1933); H. Raether, *Naturwiss.* 22, 151 (1934); W. Lochte-Holtgreven, *Naturwiss.* 22, 418 (1934).

† Wigner, *Gött. Nachr.* 374 (1927).

$(\overset{Z_1}{M_1}) + (\overset{Z_2}{M_2}) \rightarrow (\overset{Z_3}{M_3}) + (\overset{Z_4}{M_4}) + \dots$  as  $\begin{cases} \text{probable} \\ \text{not probable} \end{cases}$  if for a given relative energy of the initial particles the reaction is  $\begin{cases} \text{more} \\ \text{less} \end{cases}$  probable than a reaction

$$(\overset{Z_1'}{M_1'}) + (\overset{Z_2'}{M_2'}, \overset{Z_3'}{M_3'}) + (\overset{Z_4'}{M_4'}) + \dots,$$

whereby  $\begin{cases} Z_1' \leq Z_1 \\ Z_1' \geq Z_1 \end{cases}$  and  $\begin{cases} Z_2' \leq Z_2 \\ Z_2' \geq Z_2 \end{cases}$ . (We exclude from comparison simple capture of particles:  $(\overset{Z_1}{M_1}) + (\overset{Z_2}{M_2}) \rightarrow (\overset{Z_1+Z_2}{M_1+M_2}) + h\nu$ .)

§ 2. We shall first consider the disintegration of  $\text{Li}^6$  and  $\text{Li}^7$  by protons and deuterons because these reactions are comparatively well known. In disintegrating ordinary lithium by protons it has been found that there exist three groups of particles, two of short range and one of long range\*. For protons of about 200 kV. the short range particles are about 2 or 3 times more abundant than the long range particles. Since the disintegration of the separated Li isotopes by Oliphant, Shire and Crowther† we know that the short range particles are due to  $\text{Li}^6$  and the long range particles to  $\text{Li}^7$ , whence the reactions are‡:



As Aston's value for the relative intensities of the Li isotopes is  $\text{Li}^6 : \text{Li}^7 = 1 : 11$  the relative probabilities for disintegration of  $\text{Li}^6$  and  $\text{Li}^7$  respectively by 200 kV. protons are about 30 : 1.

This ratio cannot be explained by a different probability for a proton to enter the  $\text{Li}^6$  or  $\text{Li}^7$  nucleus. On the contrary: we might expect this probability to be larger for the  $\text{Li}^7$  nucleus, as the proton has there a slightly larger effective velocity, and the potential barrier for protons should be there somewhat lower because of the attractive forces of the extra neutron in  $\text{Li}^7$ .

Let us try to understand from our assumptions (A) and (B 1 + 2) why reaction (2) is "not probable." For this purpose we need a model of the particles involved in this reaction. We know that the spin of the proton is  $\frac{1}{2}$  (in units  $\hbar$ ) and that  $\alpha$ -particles have the spin 0 and that they obey Bose-Einstein statistics. According to Landé§ we can picture the  $\text{Li}^7$  nucleus (whose spin is  $\frac{3}{2}$  and whose Landé-factor  $g = 2.19$ ) as containing an  $\alpha$ -particle, a neutron-shell of two neutrons with opposite spins, and a "free" proton with an orbital momentum  $L = 1$  and the spin parallel to  $L$  so that the total angular momentum  $I(\text{Li}^7) = \frac{3}{2}$ . (We denote the orbital part, the spin part and the total angular momentum of a nucleus A by  $L(A)$ ,  $S(A)$  and  $I(A)$  respectively.)

\* Oliphant and Rutherford, *Proc. R.S. A*, **141**, 259 (1933).

† *Nature*, **133**, 377 (1934).

‡ Cockcroft and Walton, *Proc. R.S. A*, **137**, 229 (1932); Oliphant and Rutherford, *loc. cit.*; Oliphant, Shire and Crowther, *loc. cit.*

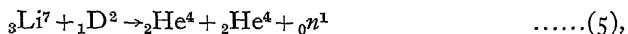
§ *Phys. Rev.* **44**, 1028 (1933).

The total angular momentum of the two resulting  $\alpha$ -particles is equal to their mutual orbital momentum  $l_2$  which can only be an *even* number\* (because of the symmetry of the  $\alpha$ -particle wave functions). From (iv) it follows that the total angular momentum of the system *before* the reaction has also to be even. If for the bombarding proton  $l_1 = 0$ , it follows that its spin has to be parallel to the spin of the "free" proton in  $\text{Li}^7$ , and therefore that one proton spin has to change its direction in order to get the closed proton shell in the second resulting  $\alpha$ -particle. Only if  $l_1 \geq 1$  no spin needs to change its direction. We can therefore conclude from (A) and (B1) that reaction (2) is "not probable."

If, however, one of the  $\alpha$ -particles in reaction (2) remains in an excited state with  $L = 1$  and  $S = 0$  or  $1$  the reaction would not be "forbidden" for  $l_1 = 0$ . These excited states might give rise to the  $\gamma$ -rays observed by Crane and Lauritsen† when bombarding lithium with 900 kV. protons. If the excitation energy is nearly the total energy available in the disintegration, the particles will have a small probability of breaking up (because of their mutual potential barrier) and the probability of getting excited  $\alpha$ -particles will rise steeply with the energy of the bombarding protons until the relative energy of the  $\alpha$ -particles (with one in an excited state) surmounts the top of the barrier of their mutual potential.

For the  $\text{Li}^6$  nucleus no vector model is known and we want here to derive one from the experimental results on artificial nuclear transformations. We assume that the  $\text{Li}^6$  nucleus is built up of an  $\alpha$ -particle and a proton and neutron. From the high probability of reaction (1) and the small velocities of the resulting particles we conclude (using (B1 + 2)) that  $l_1 = l_2 = 0$  or  $L(\text{Li}^6) = L(\text{He}^3)$ . From the reactions considered in the next two paragraphs we shall obtain more details of the  $\text{Li}^6$  model.

§ 3. We shall now consider the reactions



which may be considered as experimentally proved‡.

We picture the D nucleus as consisting of a proton and a neutron (whose spin is, as usually, assumed to be  $\frac{1}{2}$ ) with no mutual orbital momentum§ and *parallel* spins because of the observed total angular momentum  $I(\text{D}) = 1$  ||.

As reaction (3) is "probable" we infer from (B1) that  $l_1 = 0$ . In order to get the closed shell of another  $\alpha$ -particle in this reaction we conclude from (A) that the spin part of the angular momentum of  $S(\text{Li}^6) = 1$ . As the mutual angular momentum  $l_2$  of the two resulting  $\alpha$ -particles has again to be an *even* number it follows that  $L(\text{Li}^6) = \text{even number}$  and that therefore  $I(\text{Li}^6) \geq 1$ . In the next paragraph we shall show that  $L(\text{He}^3) = 0$ , and as we have shown in § 2 that  $L(\text{Li}^6) = L(\text{He}^3)$  we get

\* Cf. Beck, *loc. cit.*

† See this volume, pp. 133, 135, 139.

‡ Lewis, Livingstone and Lawrence, *Phys. Rev.* **44**, 55 (1933); Oliphant, Kinsey and Rutherford, *Proc. R.S. A*, **141**, 722 (1933); Cockcroft and Walton, *ibid.* **144**, 704 (1934).

§ E. Wigner, *Phys. Rev.* **43**, 252 (1933).

|| Lewis and Ashley, *Phys. Rev.* **43**, 837 (1933); Murphy and Johnston, *ibid.* **45**, 550 (1934).

$I(\text{Li}^6) = S(\text{Li}^6) = 1$ . From this we should expect  $\text{Li}^6$  to have a magnetic moment of the order of magnitude of the magnetic moment of the dipton. Schüler\* states that he could not find any hyperfine structure in the spectrum of  $\text{Li}^6$ , and that if any splitting exists it must be smaller than  $\frac{1}{5}$  of the splitting of the  $\text{Li}^7$  lines. As the magnetic moment of the dipton is about  $\frac{1}{5}$  of the magnetic moment of  $\text{Li}^7$ †, our conclusions about the angular momentum and the magnetic moment of  $\text{Li}^6$  are not in contradiction to Schüler's observations.

From reaction (4) we cannot draw any essentially new conclusions for the  $\text{Li}^6$  model. It is a probable reaction and this is consistent with our assumptions (A) and (B 1 + 2) and the Landé model for  $\text{Li}^7$  as the velocity of the proton arising in this reaction—which has an  $l_2 = 1$  if  $L(\text{Li}^6) = 0$ —is rather high.

In reaction (5) the difficulty of an even mutual angular momentum (cf. reaction (2)) does not occur for the resulting two  $\alpha$ -particles in the case  $l_1 = 0$ , as the neutron can carry away the superfluous angular momentum 1. We conclude then from (B 2) that quick neutrons will be more probable in this reaction than slow ones, i.e. that the  $\alpha$ -particles will have a small probability of going in almost opposite directions. In agreement with the experimental result it follows from (A) and (B 1) that reaction (5) is a probable one.

§ 4. We cannot apply our definition of probability to the reactions‡



which are about equally probable. But the experimental results suggest that these reactions are "very probable." We therefore are justified in concluding that  $l_1 = l_2 = 0$  in both these reactions. This leads to  $L(\text{H}^3) = L(\text{He}^3) = 0$  and we can infer that the three constituents of  $\text{H}^3$  and  $\text{He}^3$  respectively have the same wave functions and therefore that the two equal constituents—the neutrons in  $\text{H}^3$ , the protons in  $\text{He}^3$ —differ in their spin co-ordinates (Pauli's principle). This implies

$$S(\text{H}^3) = S(\text{He}^3) = \frac{1}{2}.$$

The magnetic moments of  $\text{H}^3$  and  $\text{He}^3$  respectively should be of the same order as those of the proton and neutron respectively.

§ 5. As a last example we consider the reactions



which are both "probable" reactions (yield higher than for proton bombardment of  $\text{Li}^7$ ). The nuclear spins of the boron isotopes are not known. Using (A), we con-

\* *Z. f. Phys.* 66, 431 (1930).

† Estermann and Stern, *Z. f. Phys.* 86, 131 (1933); A. Farkas, L. Farkas and Harteck, *Proc. R.S. A*, 144, 481 (1934).

‡ Oliphant, Harteck and Rutherford, *Proc. R.S. A*, 144, 692 (1934).

§ Oliphant and Rutherford, *Proc. R.S. A*, 141, 259 (1933).

|| Cockcroft and Walton, *Proc. R.S. A*, 144, 704 (1934).

¶ White and Lawrence, *Phys. Rev.* 43, 304 (1933).

clude from (8) and (9) that  $S(B^{11}) = \frac{1}{2}$  and  $S(B^{10}) = 1$ . Using  $(B_1 + 2)$  we infer from reaction (8) (where the mean velocities of the resulting  $\alpha$ -particles are not large) that  $L(B^{11}) = 0$ . We cannot draw a similar conclusion for  $B^{10}$  from (9) because here the resulting  $\alpha$ -particles are rather quick.

We summarize our results concerning vector models for some of the light nuclei in the following table ( $\mu$  = magnetic moment):

	$S$	$L$	$I$	$\mu$ (order of magnitude)
${}^1_1\text{H}^3$	$\frac{1}{2}$	0	$\frac{1}{2}$	$\mu(\text{H}^1)$
${}^2_2\text{He}^3$	$\frac{1}{2}$	0	$\frac{1}{2}$	$\mu(n^1)$
${}^3_3\text{Li}^6$	1	0	1	$\mu(\text{D}^3)$
${}^5_5\text{B}^{10}$	1	—	—	—
${}^5_5\text{B}^{11}$	$\frac{1}{2}$	0	$\frac{1}{2}$	$\mu(\text{H}^1)$

As the proton and neutron have parallel spins in the dipton, we might expect them to have parallel spins in those nuclei which consist of a number of closed shells (which have no directional forces) together with *one* proton and *one* neutron, especially the nuclei  $\begin{pmatrix} Z \\ 2Z \end{pmatrix}$  ( $Z$  odd) of which kind only four stable ones are known, viz.  ${}^1_1\text{D}^2$ ,  ${}^3_3\text{Li}^6$ ,  ${}^5_5\text{B}^{10}$  and  ${}^7_7\text{N}^{14}$ .  ${}^7_7\text{N}^{14}$  is known to have the spin 1.

Dr H. S. MASSEY. In connexion with the communication from Drs Bethe and Peierls I should like to point out that in January of this year Dr Mohr and I calculated the probability of combination of a proton and neutron to form a dipton. This probability can be related to that of the reverse process discussed in the above communication by purely thermodynamical methods. It is then found that our results agree substantially with those of Drs Bethe and Peierls for the cases they consider, while for other models which we have tried, a wider variation (75 per cent) in calculated values is obtained. It seems that experiment and theory agree for the photoelectric process but, if the experiments of Lea and of Fermi and his collaborators are to be interpreted as due to radiative combinations of neutrons and nuclei, there is a big discrepancy for the reverse process. As this would involve a failure of thermodynamics it would seem that the experiments on the radiation phenomena require some other interpretation.

It may be pointed out also that the range of interaction between neutron and proton assumed in Bethe and Peierls' calculations receives support from measurements of angular distributions of protons projected by neutrons.

In view of the difficulty of definitely determining the mass of the neutron it would be desirable to investigate the disintegration of the dipton by  $\alpha$ -particles. Calculations made by Dr Mohr and myself show that the probability of this process is sufficiently large to make possible an accurate determination of the minimum potential of the  $\alpha$ -particles necessary for the disintegration and hence of the binding energy of the dipton.

# COSMIC RADIATION





# FUNDAMENTAL PROCESSES IN THE ABSORPTION OF COSMIC-RAY ELECTRONS AND PHOTONS

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**ABSTRACT.** (1) We have measured 104 cosmic-ray tracks photographed by the counter-controlled cloud-chamber method, which exerts a selectivity in favour of the high-energy tracks. Between the energy limits 300 and 6000 m.e.V. the following results were found: (a) There is, as heretofore shown, approximate equality between the numbers of positive and negative particles in all energy intervals save that in the highest energy range the positives seem somewhat to predominate, thus showing that certainly the majority of the high energy particles, in so far as they represent secondaries, arise from nuclear encounters, and (b) of the 78 definitely measured energies, 71 (91 per cent) are under 4000 m.e.V., 24 (31 per cent) are under 1000 m.e.V., but out of 26 additional tracks there were 18 which we feel sure are above 4000 m.e.V., thus making the total fraction of tracks under 4000 m.e.V. 75 per cent.

(2) 2400 traversals of electrons\* with energies between 200 and 6000 m.e.V. through plates of carbon and lead, which are equivalent to one electron passage through more than 70 m. of water, or more than seven times through the earth's atmosphere, have shown numerous negatron secondaries, all of which had energies less than 300 m.e.V., and only an insignificant number of positron secondaries. Since in all these traversals there were observed no instances of impacts in the plates in which positron secondaries were produced, except for three pairs whose combined energy was less than 300 m.e.V., these facts together with (1) show that only an insignificant number of the cosmic-ray electrons at sea-level can represent the immediate secondaries of fast electrons. This conclusion depends upon the reasonable assumption that the cosmic-ray electrons passing through the atmosphere do not behave essentially differently in producing electron secondaries from those passing through our chamber.

(3) From (1) and (2) it follows that the great bulk of the sea-level cosmic-ray electrons which are of atmospheric origin can be ascribed only to photon encounters with nuclei. The above conclusion pertains only to those electrons which are of terrestrial origin; just what fraction of those in the higher range of energy represents secondaries is not yet determined, but the majority of the lower energy electrons ( $E < 1000$  m.e.V.) are undoubtedly of terrestrial origin.

(4) Abnormally high energy losses suffered by electrons of energies of the order of 100 m.e.V. show the existence of radiative electron impacts resulting in photon production. Such radiative impacts which give rise to secondary photons may account for an appreciable part of the energy loss by fast electrons.

IN a general interpretation of cosmic-ray phenomena it is important to know (1) the energy distribution of the cosmic-ray electrons\*; (2) the rate at which they lose energy in passing through matter and the way in which the energy loss is divided

\* A general term designating either positive or negative electrons, irrespective of their signs of charge, is highly desirable and the term *electron* is so used; the contractions *positron* and *negatron* are used for the sake of definiteness and brevity to denote the free positive and free negative electron respectively.

among various kinds of processes; (3) the processes involved in photon absorption. These points are particularly amenable to investigation by means of a cloud chamber magnetic field apparatus, and the present paper is a summary of some new results that we have obtained in this way.

#### § 1. THE ENERGY DISTRIBUTION OF THE COSMIC-RAY POSITIVE AND NEGATIVE ELECTRONS

The results given here include only measurements on tracks taken by means of Geiger counter-controlled expansions, such tracks having been found to be inappreciably more diffuse and to possess irregularities or distortions not much greater than the best tracks taken by the random method. The chamber was left unobstructed by metal plates, so that in most cases it was possible to use 10–11 cm. of the length of a track for curvature determination. There was no material immediately above the chamber other than about 1 cm. of brass, and the copper and iron in the apparatus itself. Checks obtained by curvature measurements on tracks taken in a low magnetic field have shown that our range of measurement extends to about  $5 \times 10^9$  e.V., and that in some isolated cases lower limits of about twice this value can apparently be established.

Out of the 104 tracks (not including shower particles or those negative electrons appearing to be ejected as secondaries from the chamber wall) 6 were completely discarded as unfit for measurement because of distortion; 20 others could scarcely be regarded as measurable, but permitted the placing of lower limits, of which 18 were greater than  $4 \times 10^9$  e.V. The remaining 78, of which 42 were positive and 36 negative, had energies below  $6 \times 10^9$  e.V., on the assumption that all of them were electrons. The energy distribution is shown in figure 1, and the energies are listed in table 1. By including the 20 tracks for which lower limits were placed to the energy, we can estimate that about 75 per cent of the particles exclusive of showers have energies less than  $4 \times 10^9$  e.V.; including the shower particles, this estimate becomes 82 per cent. The energy distribution of the 41 shower particles appearing in this set of photographs is shown in figure 2, the combined distribution for all particles in figure 3.

The differences in the energy distribution here given as compared with that previously reported are attributed, firstly, to the selective action of the Geiger-Müller counters, and secondly, to the criterion previously used in choosing the tracks for measurement. The curve of figure 1, which shows the distribution of those electrons which occurred singly in the chamber and passed through both the upper and lower counters, represents only those particles contained in a relatively small solid angle defined by the two counters. Since only a small part of the heavy material surrounding the chamber is contained in this solid angle, the electrons ejected from this material, which in general appear as showers and have a lower energy, are largely excluded from this group. The previous distribution<sup>(1)</sup>, obtained without the use of counters, represents tracks lying within a larger solid angle and includes a larger fraction of the tracks ejected from the heavy material adjacent to the

Table 1. Energies of electrons (exclusive of showers). In addition to those listed here there are to be included 6 tracks not measurable and 20 others to whose energies only lower limits could be assigned. Of these 20 tracks there were 18 whose energies were all probably above  $4 \times 10^9$  e.V.

Positive electrons m.e.V.	Negative electrons m.e.V.	Positive electrons m.e.V.	Negative electrons m.e.V.
310	340	1800	1800
350	500	1900	2300
400	670	1900	2500
420	680	2400	2500
560	780	2400	2700
700	790	2500	2700
730	860	2500	2800
780	870	2600	3200
780	930	2800	3300
780	930	3100	3600
850	970	3100	3700
930	1100	3100	3900
980	1100	3500	4600
1000	1200	3600	5000
1100	1200	3700	5900
1200	1300	3700	
1350	1400	3700	
1500	1400	4000	
1500	1500	4200	
1600	1600	4800	
1600	1700	5100	

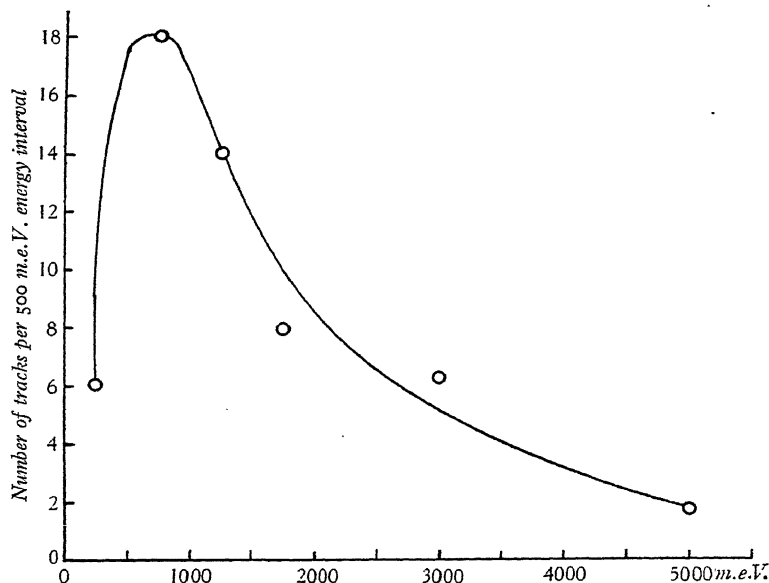


Figure 1. Energy distribution of positive and negative electrons occurring singly in the chamber.

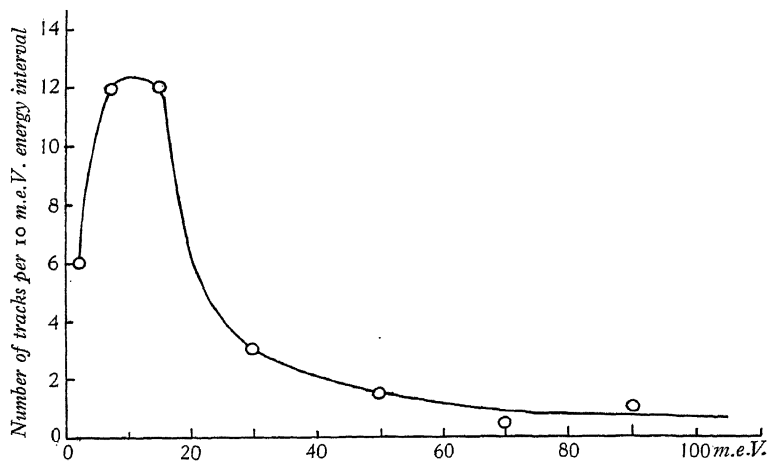


Figure 2. Energy distribution of positive and negative electrons occurring as showers in the chamber. The great bulk of these tracks were produced by secondary photon sprays.

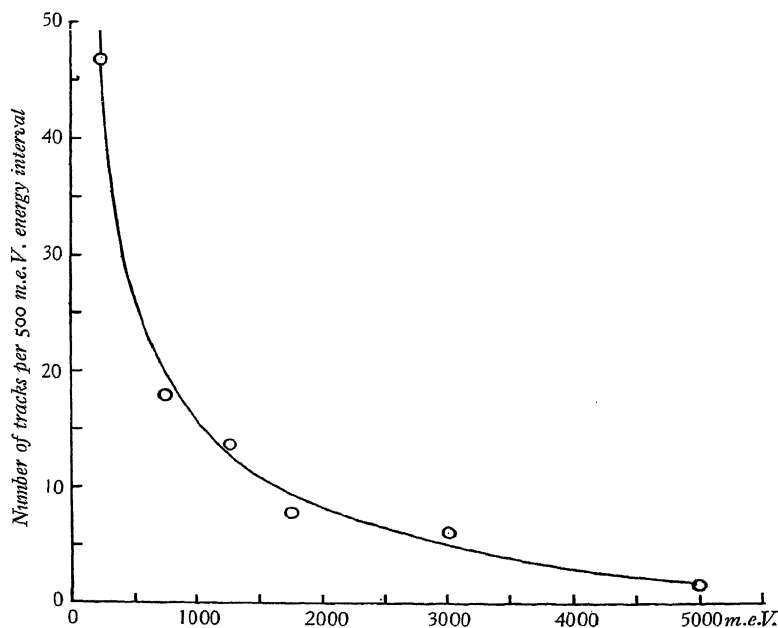


Figure 3. Energy distribution of all positive and negative electrons. The high rise of the curve at low energies is due to shower particles produced by secondary photons.

chamber. The larger number of electrons of energy greater than about 1000 m.e.V. (m.e.V. =  $10^6$  e.V.) shown by the present distribution of the single tracks is probably due to this cause. The energy distribution of the shower particles shown in figure 2 has a rather sharp maximum at about 15 m.e.V. It is the inclusion of these low energy particles which accounts for the high rise of the curve of figure 3 at low energies, since this curve includes both single tracks and shower particles. In the curve previously given, figure 5, p. 411, *Phys. Rev.* **44** (1933), only tracks of length greater than 8 cm. in the chamber were used, and the low energy tracks, most of which exhibit lengths considerably less than 8 cm., were excluded. Our first energy distribution<sup>(2)</sup> and that given by Kunze<sup>(3)</sup>, both of which include such short tracks, show a large number of very low energy electrons.

## § 2. THE PRINCIPAL MODES OF ENERGY LOSS BY HIGH ENERGY ELECTRONS

The known ways by which an electron can lose energy in passing through matter are: (1) Excitation and ionization of atoms along its path. (2) Transfers, by close encounters, of large amounts of energy to extranuclear electrons. (3) Production of electron pairs. (4) Radiative losses in nuclear collisions. The contributions made by these four processes are discussed in the following paragraphs.

### 1. *Energy loss by ionization*

This may be best investigated by making a direct count of the total number of ions produced per cm.; a knowledge of the average energy expended per ion-pair then enables us to compute the energy loss per cm. A careful investigation of the energy loss per ion (-pair) has been made by Eisl<sup>(4)</sup> with cathode rays in the energy range from 9 to 59 kV. From the total ionization produced he found for this range of energies a constant value of 32.2 for the energy loss in e.V. per ion. If we assume this value to hold approximately for the cosmic-ray electrons, an assumption which is quite well founded, and take our value of 31 ions/cm. for the total specific ionization as determined from counts made on diffuse tracks, then we obtain a lower limit of 1000 e.V./cm. for the specific energy loss, in primary ionization, by a cosmic-ray electron in standard air. It should be emphasized that the 31 ions/cm. represents only a lower limit because of the impossibility of determining the number of drops in the ion clusters along the track which result from low energy delta-rays. The inclusion of these may raise the above value as high as 45, and thus we may conclude that an electron traversing the earth's atmosphere vertically to sea-level can lose as much as 1500 m.e.V. by ionization of atoms along its path.

### 2. *The production of secondaries by close encounters with extranuclear electrons*

To determine the contribution made by (2) we have observed the passage of 2400 cosmic-ray electrons through plates of lead and carbon. From this number of primary traversals, 71 negatrons were observed in the energy range above about 1 m.e.V., as well as 3 positron-negatron pairs which had been ejected as secondaries

from the plates, the pairs appearing from the lead only. The relatively small number of positive secondaries justifies the assumption that practically all the single negative electron secondaries arise from close encounters with extranuclear electrons. A calculation of the energy distribution of the secondaries which should be observed below a thick plate, made from the theoretical differential cross-section given by Carlson and Oppenheimer<sup>(5)</sup> for such encounters, shows that both the absolute number of secondaries and their energy distribution agree satisfactorily with theory, if we assume that the primary particles traversing the plates are electrons. The formula given by Carlson and Oppenheimer for the probability that a primary electron with energy  $\epsilon_0$ , in traversing a plate of thickness  $t$  with  $n$  extranuclear electrons per cm<sup>3</sup>, will produce a secondary with energy  $\epsilon$  in the interval  $d\epsilon$ , may be written in the form

$$p(\epsilon, \epsilon_0) d\epsilon = \frac{\pi n e^4 t}{2 m^2 c^4} \cdot \frac{\epsilon^4 + \epsilon_0^4 + (\epsilon_0 - \epsilon)^4}{\epsilon^2 \epsilon_0^2 (\epsilon_0 - \epsilon)^2} d\epsilon,$$

where  $\epsilon$  and  $\epsilon_0$  are expressed in multiples of  $2mc^2$ , or approximately in m.e.V., and must satisfy the conditions  $\epsilon_0 \gg \frac{1}{2}$ ;  $\epsilon_0 \geq 2\epsilon$ . In the experimental data used for comparison with theory, only those primaries have been considered for which  $\epsilon_0 \geq 200$ . With this restriction, since for most of those primaries  $\epsilon_0 \gg 200$ , the condition  $\epsilon_0 \gg \epsilon$  is well satisfied in the range below, say  $\epsilon = 100$ , and the above formula reduces simply to

$$p(\epsilon, \epsilon_0) = \frac{\pi n e^4 t}{m^2 c^4} \cdot \frac{1}{\epsilon^2},$$

to which approximation it has been given by other writers.

If we assume (1) that the primaries traverse the plate normally, a condition which is nearly satisfied, (2) that the angle between secondary and primary is small, a condition sufficiently well satisfied for  $\epsilon > 5$ , and take for the range of the secondaries  $R = \alpha\epsilon$ , where  $1/\alpha$  is the energy loss per cm., then we find for the distribution in energy of the secondaries emerging below a plate of thickness  $t$ , when traversed by  $N$  primaries,

$$f(\epsilon) = \frac{\pi n e^4}{m^2 c^4} \cdot \frac{N t}{\epsilon (\epsilon + t/\alpha)}.$$

$1/\alpha$  was determined by measuring directly the energy lost by electrons in traversing the plate, and was found to have for carbon a mean value of about 5 m.e.V./cm. Since this value is based upon only four observations, 6.8, 6.0, 3.5 and 3.9 m.e.V./cm. for electrons having an initial energy from 12 to 34 m.e.V., it is only approximate. Prof. Millikan has pointed out to us that the 6000 m.e.V. given by Bowen, Millikan and Neher<sup>(18)</sup> for the energy lost by an electron in traversing the earth's atmosphere leads to a value of  $1/\alpha$  equal to 13 for carbon, if we make the assumption that the mean energy loss is the same for electron energies of 10 to 50 m.e.V. as for 6000 m.e.V. In figure 4 is shown the experimentally determined distribution for a 1.5 cm. carbon plate. Three theoretical curves are shown, for  $1/\alpha = 5$ ,  $1/\alpha = 13$  and  $1/\alpha = 0$ . In figure 5 are given the results for a 1 cm. lead plate, with the theoretical curve plotted for two values of  $\alpha$ , the better fit being

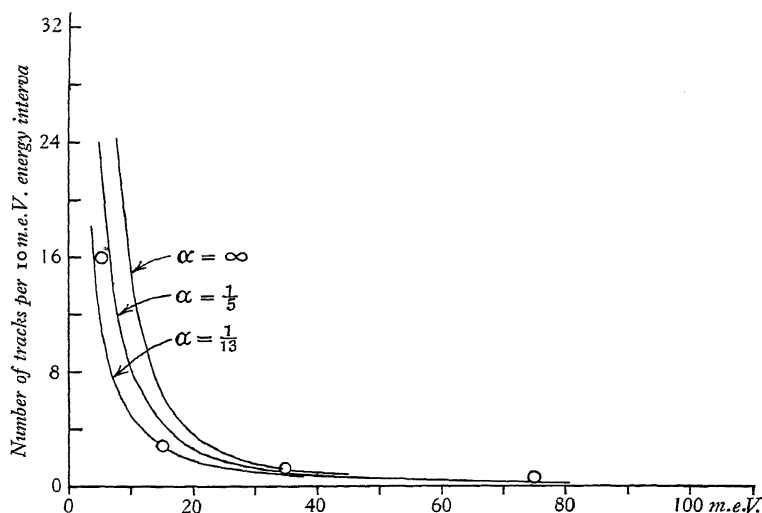


Figure 4. Experimental points are plotted as circles. The two lower curves are theoretical distributions corrected for energy loss in the plate; the upper curve the uncorrected theoretical distribution. Energy distribution of secondary negative electrons from 1.5 cm. carbon. 587 traversals 26 secondaries.

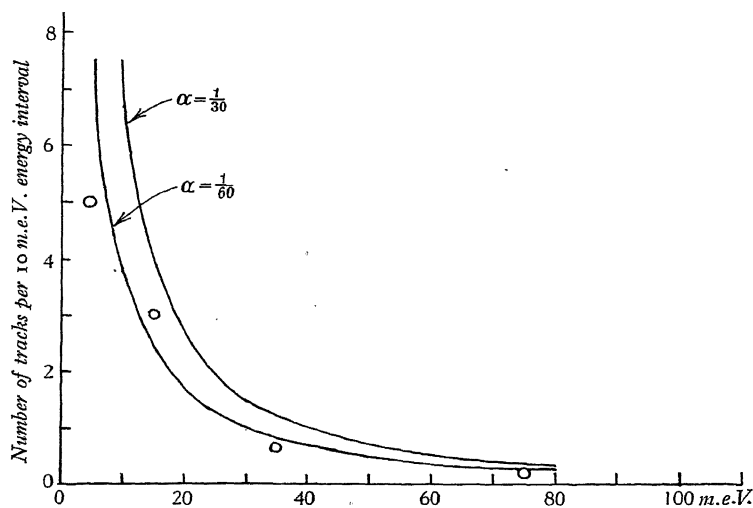


Figure 5. Experimental points are plotted as circles. The curves are theoretical distributions corrected for energy loss in the plate. Energy distribution of secondary negative electrons from 1.0 cm. lead. 407 traversals, 11 secondaries.



obtained with  $\alpha = \frac{1}{60}$ , which agrees well with our determination of the mean energy loss in lead, about 57 m.e.V./cm. (See section below on energy loss in lead.)

In view of the approximate agreement between the above experimental facts and existing theory, the latter may be used to estimate the total loss in energy undergone through transfers to extranuclear electrons, by a primary electron which traverses the whole of the earth's atmosphere vertically. Carlson and Oppenheimer have given the cross-section in integrated form, which is, in our notation,

$$\text{Loss/cm. (transfers } > \epsilon_1) = \frac{\pi ne}{m^2 c^4} \log \frac{\epsilon_0}{4\epsilon_1} + \frac{9}{2} \\ \epsilon_1 \gg I/2mc^2,$$

where  $I$  is of the order of the mean ionization potential.

Thus for a  $10^{10}$  e.V. electron, and considering individual transfers greater than  $\epsilon_1 = 0.001$  ( $10^3$  e.V.), we find the energy loss per cm. from the above cause to be 1500 e.V. in standard air, or 1300 m.e.V. for the whole atmosphere. This result is not critically dependent on the value of  $\epsilon_0$ , nor on the choice of  $\epsilon_1$ .

### 3. Formation of electron pairs by cosmic-ray electrons

The theory of pair formation by electrons as developed by Furry and Carlson<sup>(6)</sup> has not as yet given sufficiently definite results to permit a satisfactory comparison between them and the experimental data. With the few such pairs so far obtained a rough experimental estimate, 1.0 m.e.V./cm., can be given for the total contribution to energy loss in lead by pairs with energies in the range above, say, 15 m.e.V. No pairs have been observed from carbon and the total contribution to energy loss is probably of considerably less importance in carbon than in lead. The possibility that these pairs from the lead may have resulted from the absorption of photons given off in radiative collisions should not be overlooked. Further data are needed to draw any very definite conclusions except that the contribution made by pair formation to the total energy loss, even in lead, is unimportant compared with that made by other causes.

### 4. Energy loss in lead: radiative losses

We have previously reported<sup>(1)</sup> as a preliminary estimate approximately 35 m.e.V./cm. in lead as the mean observed energy loss for electrons up to 300 m.e.V. energy. As pointed out at that time, the data were not extensive enough to enable an accurate mean value of energy loss to be given because of the large fluctuations among the values of energy loss then measured. Our subsequent measurements have shown even greater fluctuations, and we have interpreted the higher energy losses as due to radiative impacts in which photons were produced<sup>(7)</sup>. It is not possible by direct curvature measurements of the electrons in the magnetic field before and after they penetrate 1 cm. of lead to determine the energy loss by very fast electrons, because of their small curvature. We have observed several cases in which the specific energy loss in lead could be accurately determined by measurement of the track curvature before and after the electron traversed the lead plate. The results are listed in table 2.

Table 2. Energy loss in lead

Sign of charge	Initial energy m.e.V.	Final energy m.e.V.	Energy loss m.e.V.	Thickness traversed cm.	Specific energy loss m.e.V./cm.
—	113	86	27	1.35	20
—	240	220	20	1.1	18
—	220	160	60	1.1	55
+	38	6	32	1.1	29
+	63	23	40	0.7	57
+	200	125	75	1.1	68
+	140	20	120	1.0	120
—	106	26	80	1.0	80
—	110	12	98	1.5	65

There are in addition several cases in which the specific energy loss could not be accurately determined, but limits could be placed on the energies before and after the electron penetrated the plate, of such values that the specific energy loss must have exceeded 100 m.e.V./cm., and in a few cases probably a few hundred

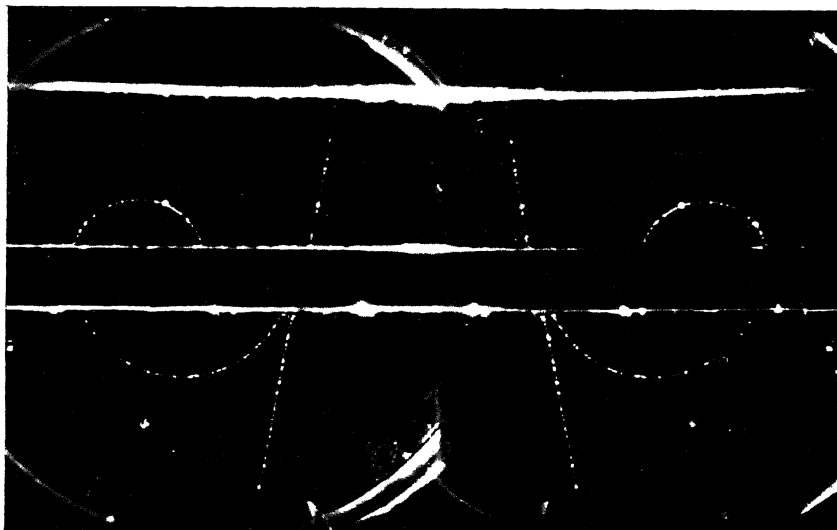


Figure 6. 19,000 gauss. The left-hand view is the direct chamber image; the right-hand view a mirror image for stereoscopic purposes. A secondary negatron results from a close encounter with an extranuclear electron in carbon. The negatron loses 5.6 m.e.V. in traversing the 1.5 cm. carbon plate.

m.e.V. Figure 6 of our previous publication<sup>(8)</sup> is an example of a positron losing 120 m.e.V. in traversing 1 cm. of lead. One of the photographs by Blackett and Occhialini<sup>(9)</sup> also shows a case in which the specific energy loss exceeds 100 m.e.V. per cm. of lead.

There are two possible interpretations of these large energy losses on the basis

of absorption by extranuclear electrons, both of which are untenable: (1) The production by close encounters of a large number of secondary negatrons with energies insufficient for them to emerge from the plate, or (2) the transfer of considerable amounts of energy to a few electrons. That the first possibility is exceedingly improbable is shown by our statistical study of the frequency of production of secondary electrons. The second possibility is immediately ruled out by the fact that high energy electron secondaries, which are always ejected at a small angle with the primary electron track, would penetrate the plate and appear in the photographs. Furthermore, the large energy losses cannot be explained by

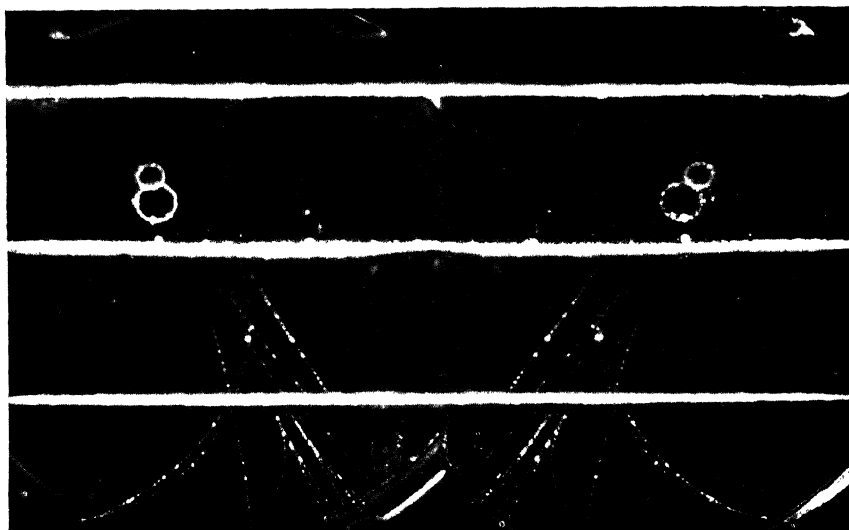


Figure 7. 19,000 gauss. From the lower plate (1.5 mm. lead) a group of four electrons, two positive and two negative, is ejected by a secondary photon. Their energies are: negatives, 13 m.e.V. and  $\sim 390$  m.e.V.; positives, 5 m.e.V. and  $\sim 220$  m.e.V. Immediately to the right of this group of four tracks is shown also one of the three observed cases of pair production by a fast electron. The incoming electron produces a pair in the lower 1.5 mm. lead plate; both the positive and negative components have energies of 110 m.e.V. A low energy electron-pair is represented by the "figure 8" in the upper part of the chamber.

the direct production within the plate of complex positron-negatron showers by the incoming particles, since in no case, out of more than 2300 traversals of carbon and lead plates, have electrons been observed to produce such showers. Some medium for carrying off the excess energy, which does not produce a track, is required, and the only reasonable assumption is that by a nuclear impact in the lead one or more photons are produced. The photograph in figure 8 exhibits the track of a negative electron with more than 20 m.e.V. energy, which stereoscopic examination proves to have been stopped in a lead plate only 1.5 mm. thick. An alternative possibility that it could have been scattered out of view nearly parallel to the plate is so remote that it may at once be discarded. It is not possible with the present experimental data to determine the ratio of the energy loss by electrons due to radiative collisions

to that due to ionization, as a function of the energy of the electron, nor to state the dependence of this ratio on the atomic number of the absorber.

A calculation made by Heitler and Sauter<sup>(10)</sup> shows that owing to radiative losses alone, a beam of 100 m.e.V. electrons should have an "absorption coefficient" of about  $3.0 \text{ cm}^{-1}$  of lead; 1000 m.e.V. electrons should have an even greater absorption coefficient, about  $4.0 \text{ cm}^{-1}$  of lead, or a mean range of 0.25 cm. in lead. While the data presented above give evidence for the existence of rather large radiative losses, they constitute as well strong evidence for the breakdown of the theoretical formula in the energy range above 100 m.e.V. Prof. Oppenheimer has kindly pointed

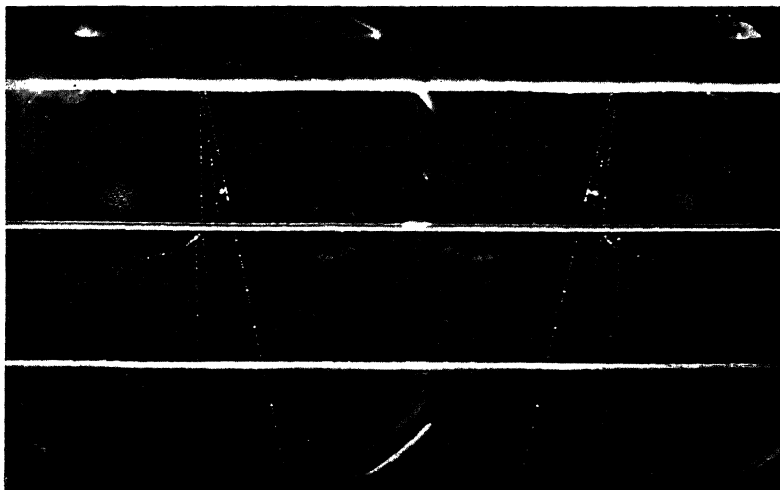


Figure 8. 900 gauss. From the 1 cm. lead plate in the top portion of the chamber three electrons are ejected. The central one, a negatron of 20 m.e.V. energy, is proved by stereoscopic vision to be stopped in the 1.5 mm. lead plate placed across the centre of the chamber, presumably transferring its energy to a photon. The other two electrons pass through the plate, one producing a low energy secondary track in an encounter with an extranuclear electron. A single negatron of energy greater than 30 m.e.V. is simultaneously ejected from the same central lead plate by a photon which probably originated in the lead above the chamber.

out to us that the screening of the nucleus by the outer electrons, which was not taken into account in the above theory, may appreciably modify the results. Although no detailed comparison can be made with the theory, the penetrating power of the cosmic-ray electrons in lead as shown by cloud chamber experiments is greater than that permitted by the theory in its present form in which screening is neglected\*.

\* In a paper which has just appeared (*Proc. R.S. A*, 146, 83 (1934)) Bethe and Heitler have presented detailed calculations of the theoretical radiative losses undergone by high energy electrons, which take account of the screening of the nucleus and yield penetrating powers considerably greater than did the preliminary results given by Heitler and Sauter. Nevertheless, the new theoretical values for the mean radiative loss in lead (177 m.e.V./cm. for 100 m.e.V. electrons and 550 m.e.V./cm. for 300 m.e.V. electrons, the latter value becoming 250 m.e.V./cm. for a 1 cm. lead plate if the dependence of the probability of a radiative loss on the energy of the electron is taken into account) still seem to be too high to be reconciled with our experimental data, although the latter contain as yet too few cases where accurate measurements are possible, for a satisfactory comparison to be made.

*Nature of the cosmic-ray particles.* Williams<sup>(11)</sup> has suggested that the high energy cosmic-ray particles may consist of positive and negative protons rather than electrons. The following two observations based on our data bear on this question.

(a) It was shown above that the number and distribution in energy of the negatrons ejected as secondaries by particles traversing plates of lead and carbon agree with those to be expected theoretically for extranuclear encounters if the incoming particles possess electronic mass. On the other hand, the assumption that the incoming particles possess protonic mass, and have the curvature distribution in the magnetic field given above, would lead to an electron-secondary energy distribution noticeably different from that actually found.

Our energy distribution of the incoming electrons shows that, exclusive of showers, about 25 per cent of the cosmic-ray particles observed in our apparatus have energies greater than 4000 m.e.V. if they are electrons, or greater than 3000 m.e.V. if they are protons. The maximum energy  $\epsilon$  in m.e.V. that a proton with energy  $\epsilon_p$  expressed in units of 1000 m.e.V. can transfer to an electron at rest is, to a good approximation for the energies here considered,

$$\epsilon = \epsilon_p (\epsilon_p + 2).$$

A 3000 m.e.V. proton, then, can transfer a maximum energy of 15 m.e.V. to an electron. A 9000 m.e.V. proton is required to produce the highest energy electron secondary ( $\sim 100$  m.e.V.) that we have observed, and would give a secondary electron distribution practically indistinguishable from that actually found. If, then, the assumption that the primary particles are protons is to be made consistent with our observed data, we must assume that through a statistical fluctuation, the 25 per cent of the primaries with energies greater than 3000 m.e.V. produced not less than 100/25 or four times as many secondaries in the energy range above 15 m.e.V. as they should on the average. Although the total number observed in this range was only 11, nevertheless a fluctuation of the above magnitude is rather improbable.

(b) A second point is that an appreciable fraction of the primary particles should pass through the atmosphere at such angles that when they pass through the cloud-chamber their energy would be sufficiently low to distinguish protons from electrons with certainty. It is significant that among some 2000 electron tracks taken by the random method, under which condition tracks passing vertically through the chamber were not favoured over those passing horizontally, there were not more than two or three low energy tracks which could with reasonable certainty be ascribed to protons.

The above considerations, which are of a statistical nature, and are necessarily subject to the gathering of further data, tend to favour the view that most of the high energy cosmic-ray particles at sea-level have electronic mass. If further data prove this view to be correct then it is obvious that the present theory of radiative losses by electrons must be inapplicable in the range of very high energies\*.

\* The suggestion made by Williams is based upon two discrepancies which exist if the cosmic-ray particles are assumed to be electrons; firstly, a discrepancy between the theoretical and observed values of primary ionization, and secondly, between calculated probabilities of radiative losses and the observed penetrating power of the particles. Neither of the theoretical formulae has been given an experimental test adequate to prove its validity in the energy range under consideration. Bowen, Millikan and Neher<sup>(18)</sup> have found that the rays sensitive to the earth's magnetic field

## §3. ABSORPTION OF PHOTONS

Experiments on photon absorption for energies up to 12 m.e.v. are in good accord with theoretical predictions. The energies and the relative numbers of positrons and negatrons ejected by  $\gamma$ -rays of Th C", as shown by our experiments<sup>(12)</sup> and by those of Chadwick, Blackett and Occhialini<sup>(13)</sup>, and the values of absorption coefficients in various elements both of the Th C"  $\gamma$ -rays and those resulting from

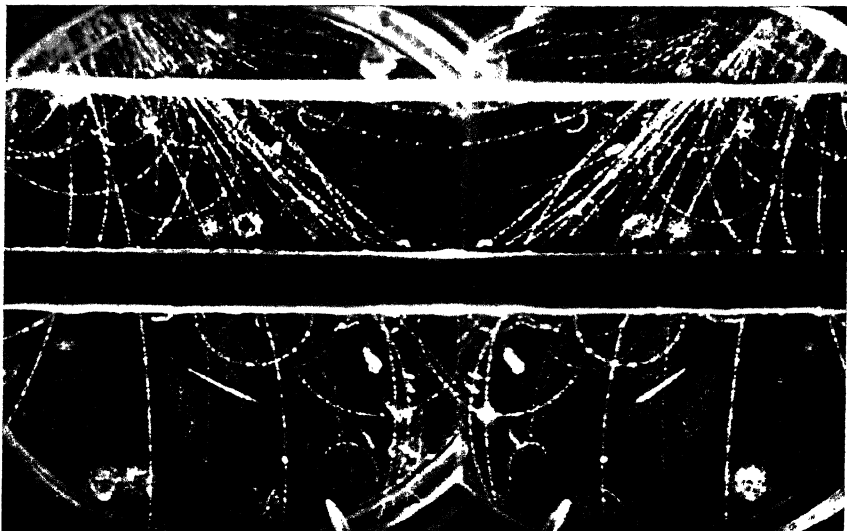


Figure 9. 12,000 gauss. A complex electron shower. Some cases of secondary photon absorption resulting in low energy showers occur in the upper 1.5 mm. lead plate. The central plate is 1.5 cm. carbon.

the annihilation of the positrons, combine to show the success of the Dirac theory as developed by Oppenheimer and Plesset and by Heitler and Sauter, in interpreting the results obtained for photon energies of 2.6 m.e.v. Recently Crane, Delsasso, Fowler and Lauritsen<sup>(14)</sup> have used  $\gamma$ -rays up to 12 m.e.v. arising from the bombardment of lithium with protons and report also for rays of this energy, results in concordance with the theory.

possess an apparent absorption coefficient of about 1.0 per metre of water. If these field-sensitive rays are mainly incoming electrons, as all data strongly indicate, it then appears difficult to reconcile the highly absorbable character of these rays with the apparently small degree of interaction between the particles and the plates of lead and carbon in our cloud chamber. Since the values of  $H\rho$  of many of the particles observed in the chamber ( $5 \times 10^6$  to  $20 \times 10^6$  gauss cm.) lie in the same range as do those of the particles excluded by the earth's field, the absence of a large number of secondaries produced in the plates, either electrons or photons, may indicate a difference in character between the high energy particles observed in the cloud chamber and those incoming particles constituting the field-sensitive portion of the cosmic-ray beam. The data, however, are preliminary and for the purposes of discussion in this report we have assumed the high energy particles traversing our plates to be practically all electrons.

In the range of higher energies, experimental data which give both the energy of the photon and its penetrating power are very meagre. The presence in the cosmic rays of some kind of secondary non-ionizing rays which give rise to electron showers was first suggested by our earliest photographs and beautifully brought into evidence by the photographs of Blackett and Occhialini<sup>(9)</sup>. Our subsequent photographs<sup>(8)</sup>, which have revealed many cases in which such non-ionizing rays were absorbed by electron-shower formation in plates of lead placed in the chamber, have afforded strong evidence that the non-ionizing rays were to be identified with photons, many

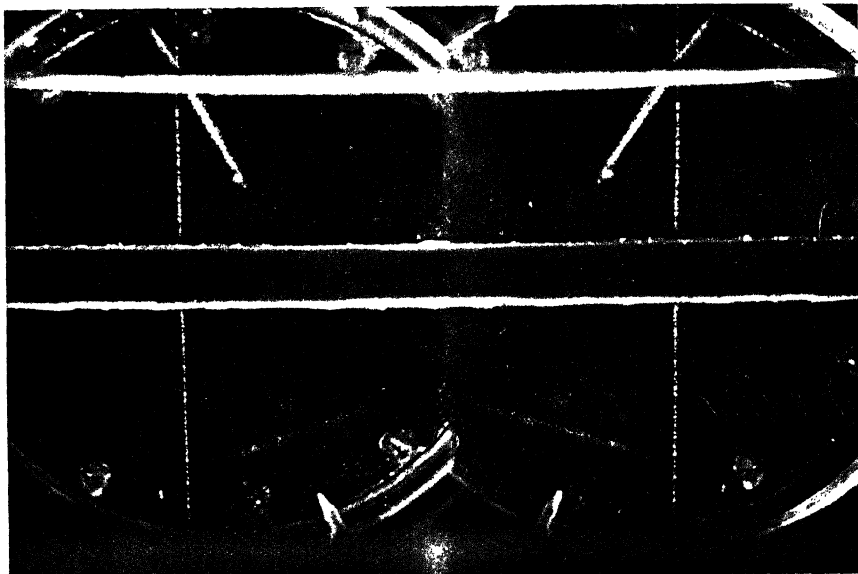


Figure 10. 12,000 gauss. An example of one of the rare instances of the observation of a heavily ionizing particle associated with cosmic radiation. The heavy track piercing the 0.25 mm. lead plate in the upper region of the chamber has an  $H\rho > 10^6$  gauss cm. and shows at least four times the ionization of a fast electron. The diffuseness of the track shows that the particle passed through the chamber before the passage of the fast electron which also appears in the photograph. It is not possible to identify the particle, but the assumption that it is a proton of 50–100 m.e.v. energy or a higher energy  $\alpha$ -particle is quite consistent with the information presented by this photograph. The fact that it penetrates the 0.25 mm. lead plate precludes the possibility that it can represent an  $\alpha$ -particle arising from contamination in the chamber.

of which were proved to be of secondary origin, ranging in energy from below 1 m.e.v. to several hundred m.e.v.

Observations with lead and carbon plates in the chamber showed the photons to be highly absorbable in a heavy element like lead and much less absorbable in a light element like carbon. Rossi<sup>(15)</sup>, Fünfer<sup>(16)</sup> and Gilbert<sup>(17)</sup>, by tube-counter experiments, have measured the absorption coefficient of the shower-producing rays, which are in all probability from comparison with the cloud-chamber experiments to be identified with the secondary photons. Gilbert finds approximately a  $Z^2$  absorption law for these rays and a coefficient about  $0.4 \text{ cm}^{-1}$  of lead. Experi-

ments of this type do not permit an estimate of the photon energy to be made except in so far as they give a measure of the range of the ejected electrons. This range is of the order of 2 cm. in lead, which corresponds to an electron energy of at least 40 m.e.V., and because three or more such electrons are required to actuate the three counters, the energies of the photons themselves are apparently of the order of at least 120 m.e.V. The energy distribution of the shower particles resulting from secondary photon sprays, given in figure 2, shows a peak at about 15 m.e.V. and suggests most probable energies for the individual shower particles somewhat less, but of the same order of magnitude, as do the tube-counter experiments. Heitler and Sauter<sup>(10)</sup> have calculated an absorption coefficient for pair production by photons, which increases with energy, and which has a value about  $1 \text{ cm}^{-1}$  of lead for 100 m.e.V. photons. The complexity of the cosmic-ray phenomena does not permit a rigorous comparison to be made between observed and calculated penetrating power of the secondary photons, but the experimental absorption coefficient of  $0.4 \text{ cm}^{-1}$  of lead indicates that while the actual penetrating power of photons of the order of 100 m.e.V. seems to agree in order of magnitude with that demanded by theory, yet it may be somewhat greater.

#### § 4. EVIDENCE THAT THE GREAT BULK OF THE COSMIC-RAY ELECTRONS OF ATMOSPHERIC ORIGIN ARISE FROM PHOTON ENCOUNTERS

The curvature measurements on cosmic-ray particles between the limits 300 and 6000 m.e.V. given in (§ 1) showed an approximate equality between the positives and negatives in all energy intervals, save that in the highest energy range the positives seemed somewhat to predominate. The positive particles in this group, in so far as they represent secondaries, must all have originated from nuclear encounters. The data on electron traversals through plates of carbon and lead given in table 3 show that the probability of producing directly a secondary electron by a

Table 3

Material and thickness of plate	Number of electron traversals	Number of secondary negatrons	Number of secondary positrons
1.5 cm. carbon	810	38	0
1.0 cm. lead	397	15	2 pos.-neg. pairs
1.1 cm. lead	176	7	0
0.2 cm. lead	267	3	1 pos.-neg. pair
0.025 cm. lead	789	8	0

nuclear encounter is very small. In a total of 2439 traversals, electrons were observed to penetrate a total of 1215 cm. of carbon and 663 cm. of lead. This corresponds to an equivalent of 24 m. of water for the carbon and 52 m. of water for the lead if it is assumed that the probability of producing a secondary per nucleus encountered is proportional to  $Z$ . If this probability is proportional to  $Z^2$  then the 663 traversals through lead are equivalent to 520 m. of water. These observations



then altogether represent the equivalent of an electron traversal through at least 76 m. of water or more than seven times through the earth's atmosphere. In all these traversals there were observed in addition to the negatron secondaries, all of which had energies less than 300 m.e.V., no positron secondaries except three cases of electron pairs from the lead, whose combined energy was less than 300 m.e.V. The fact that in all these traversals, equivalent to an electron passage at least seven times through the earth's atmosphere, there were no instances of an electron impact in which high energy ( $E > 300$  m.e.V.) secondaries of either positive or negative sign were produced, is very strong evidence that only an insignificant number of the cosmic-ray electrons at sea-level can result directly from electron impacts in the atmosphere or other absorbing material. This conclusion depends upon the reasonable assumption that the cosmic-ray electrons passing through the atmosphere do not behave essentially differently in producing electron secondaries, from those observed in the chamber.

It is concluded from the above facts that practically all of the cosmic-ray electrons at sea-level, in so far as they are of terrestrial origin, can be ascribed only to photon encounters with nuclei.

The latitude dependence and the altitude dependence of the cosmic rays show, as pointed out by Bowen, Millikan and Neher<sup>(18)</sup>, that the energy needed by an electron to traverse the earth's atmosphere to sea-level is on the average greater than 6000 m.e.V. From the data given in parts 1, 2, 3, and 4 of Section II of this paper it is clear that for an electron traversing the earth's atmosphere; the loss of energy due to ionization along its path and to the direct production of secondary positrons and negatrons is insufficient to account for much more than about half of this 6000 m.e.V. The remainder of the energy loss, which may represent the greater part of it, can be ascribed only to photon production through radiative impacts. The cloud-chamber photographs show that the secondary photons are ejected in a direction very closely parallel to that of the incoming electron which produces them, and hence the electron showers produced in the absorption of these photons will evince an east-west effect as do the incoming electrons themselves. Korff<sup>(20)</sup> and Bowen, Millikan and Neher<sup>(18)</sup> have shown that a large fraction of the electrons which exhibit an east-west asymmetry must be identified with secondary electrons produced in the atmosphere by the incoming primary electrons. The present experiments provide evidence that the bulk of the secondary electrons arise through the absorption of photon intermediary rays which are produced in radiative impacts by the incoming primary electrons. Johnson<sup>(19)</sup>, by using a tube-counter arrangement sensitive only to showers, has found an east-west asymmetry in the shower-producing rays themselves. This result can be interpreted in the above way in terms of the action of photon intermediaries.

In conclusion we wish to thank Mr William H. Pickering for providing us with the Geiger-Müller counters and the vacuum-tube apparatus. It is a pleasure also to express our great indebtedness to Prof. R. A. Millikan and to the Carnegie Corporation of New York; the latter provided funds (administered through the Carnegie Institution of Washington) which have made this work possible.

## REFERENCES

- (1) ANDERSON. *Phys. Rev.* **44**, 406 (1933).
- (2) ANDERSON. *Phys. Rev.* **41**, 405 (1932).
- (3) KUNZE. *Z. f. Phys.* **80**, 559 (1933).
- (4) EISL. *Ann. d. Phys.* **3**, 277 (1929).
- (5) CARLSON and OPPENHEIMER. *Phys. Rev.* **41**, 763 (1932).
- (6) FURRY and CARLSON. *Phys. Rev.* **44**, 237 (1933).
- (7) ANDERSON and NEDDERMEYER. *Phys. Rev.* **46**, 325 (1934).
- (8) ANDERSON, MILLIKAN, NEDDERMEYER and PICKERING. *Phys. Rev.* **45**, 352 (1934).
- (9) BLACKETT and OCCHIALINI. *Proc. R.S. A*, **139**, 699 (1933).
- (10) HEITLER and SAUTER. *Nature*, **132**, 892 (1934).
- (11) WILLIAMS. *Phys. Rev.* **45**, 729 (1934).
- (12) ANDERSON and NEDDERMEYER. *Phys. Rev.* **43**, 1034 (1933).  
ANDERSON. *Nature*, **133**, 313 (1934); *Naturwiss.* **22**, 293 (1934).
- (13) CHADWICK, BLACKETT and OCCHIALINI. *Proc. R.S. A*, **144**, 235 (1934).
- (14) CRANE, DELSASSO, FOWLER and LAURITSEN. *Phys. Rev.* **46**, 531 (1934).
- (15) ROSSI. *Z. f. Phys.* **82**, 151 (1933).
- (16) FÜNFER. *Z. f. Phys.* **83**, 92 (1933).
- (17) GILBERT. *Proc. R.S. A*, **144**, 559 (1934).
- (18) BOWEN, MILLIKAN and NEHER. This volume, p. 206.
- (19) JOHNSON. *Phys. Rev.* **45**, 569 (1934).
- (20) KORFF. *Phys. Rev.* **46**, 75 (1934).

# THE LATITUDE EFFECT FOR COSMIC RAYS

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*ABSTRACT.* It is remarked that the effect of the earth's magnetic field on cosmic rays is of importance because of the information that its study gives on their nature. The cosmic radiation cannot originally consist of uncharged radiation, since the effect of the earth's field on the secondary radiation would be less than the observed effect.

Whilst electronic particles are passing through the earth's atmosphere, their energy is diminished by about  $4 \times 10^9$  e.V., so that particles with less than this initial energy do not reach sea-level at all.

Experiments on the number of particles arriving vertically at different points between magnetic latitude  $45^\circ$  N. and  $38^\circ$  S. are described. The outfit consisted of three Geiger-Müller counters with their axes parallel, mounted in a box which could be rotated. In two of the outfits, two blocks of lead each 10 cm. thick could be placed between the counters, and in the third, the counters were close together.

It was found that in the former case there was a 13 per cent decrease, and in the latter a 16 per cent decrease in the number of vertical rays between the latitudes  $0^\circ$  and  $40^\circ$ . The number of coincidences with and without the lead screen is independent of latitude, the ratio in all cases being about 1.5. The proportion of very penetrating particles also remained constant at about 30 per cent of the total radiation.

As regards the distribution about the E.-W. line, the effect of rotating apparatus no. 1 shows a distinct asymmetry. This is interpreted as showing that the greater part of the primary particles are positively charged.

## § 1. THEORETICAL INTRODUCTION

THE influence of the Earth's magnetic field upon the cosmic rays is of great importance, because of the information that a study of this matter can give us as to the nature of these rays, and above all, of their nature when they are still far from the Earth's surface, before they have penetrated its atmosphere. Thus it seems that the problem: "Are the cosmic rays electrically charged before they enter the atmosphere?" must be answered in the affirmative, principally because of the results obtained by measuring the influence of the latitude of the place of observation upon the rays reaching it. The second question is that of the sign of these electric charges; here, while the influence of the Earth's magnetic field does not entirely solve the problem, it gives us valuable indications. Finally, we shall also obtain important information concerning the amount of kinetic energy possessed by these particular charges. I do not want here to go into a theoretical discussion of the effects of the Earth's magnetic field upon electrons, but merely to give a concise account of the results, and to compare them with the results of experiment.

*The chief hypotheses*

1. We will briefly examine the hypothesis which postulates the arrival in the Earth's atmosphere of uncharged radiation (electromagnetic or otherwise). In the course of their passage through the atmosphere these rays produce charged corpuscular rays (doubtless electronic in nature) which are the only ones we can observe. These are also the only rays which are affected by the terrestrial field; the latter bends these rays, and as a result, diverts them from their original direction. No doubt, as Rossi has pointed out, there would thus be some disparity between the intensity of a corpuscular ray arriving on the ground from the east as compared with one coming from the west, a disparity which would depend in degree upon the strength of the horizontal component of the field. But this disparity would be slight even if all the corpuscles had the same sign (which is certainly not the case). In any event, owing to the weakness of the Earth's magnetic field and the shallowness of its atmosphere (say 100 km.) no influence could affect the total number of penetrating corpuscular rays reaching different points on the Earth.

2. If, on the contrary, we suppose that the radiation which meets the upper limits of the atmosphere is already corpuscular by nature and charged, then the influence of the Earth's field becomes great because of the very long path taken by the charges within it. The matter has been mathematically treated by Störmer, Lemaitre and Vallarta, also by Rossi and Fermi. The conclusions arrived at are not very easy to summarize. However, if we assume an isotropic distribution of the directions of the rays at a great distance from the Earth, we find that for each group of particles of the same sign and of the same value of  $H\rho$  (magnetic rigidity) there is at every point of the Earth's surface a cone separating the directions from which the rays can arrive and the rest of space, which is empty. This cone has the magnetic parallel for its axis, it points towards the west or the east according as the particles are charged positively or negatively, and its semi-vertical angle depends upon the value of  $H\rho$  and upon the magnetic latitude. For a given value at that latitude the rays of less than a certain minimum  $H\rho$  do not reach the Earth at all; for increasing values of  $H\rho$  the cone containing the possible directions of arrival opens progressively and covers the whole of space, going from east to west for negative particles. For a given rigidity the cones open from the maximum latitude that this radiation can attain, up to the magnetic poles. In the interiors of all the possible cones the density of the particles is the same as the density they would have in the absence of the magnetic field, as Lemaitre and Vallarta as well as Fermi and Rossi have shown.

3. Absorption while passing through the terrestrial atmosphere also makes the phenomenon more complicated by diminishing the energy of the electronic particles by about  $4 \times 10^9$  e.V. That is to say, particles possessing less than this minimum energy do not reach sea-level, but they can be found at greater heights—at least in the low latitudes where they are allowed to arrive.

The complete application of these results to a radiation coming to the Earth

from all directions, and possessing a continuous energy spectrum, gives rise to the establishment of curves of the variation of the cosmic rays with latitude, which naturally depend considerably upon the particular spectrum distribution which is adopted. A theory due to Clay assumes that this distribution is Maxwellian.

#### *Variation of total ionization*

Whatever the form of distribution adopted, the foregoing conclusions point to a variation in the total number of particles reaching the ground, depending upon the latitude of the point of observation. In fact, as we proceed from one magnetic pole towards the equator, the solid angles in which corpuscles of various velocities arrive, diminish progressively, and the total ionization due to all the corpuscles—nearly proportional to their number—should decrease. In reality the diminution does not begin at the pole if one observes it at sea-level, for the rays which would be the first to undergo a diminution, not being sufficiently penetrating, do not reach the earth at all, and play no part at this level. The falling-off begins with the particles which possess the minimum energy required for them to pass through the earth's atmosphere. At higher altitudes the falling-off begins at lower latitudes. This is exactly what the experiments of Clay, Compton and their collaborators, carried out with ionization chambers, have shown. From these observations we can assume that the distribution of energies includes at least from  $4 \times 10^9$  to  $6 \times 10^{10}$  e.V.

#### *Variation in the number of particles*

We can seek to measure at points on different latitudes, not the effect of the whole of the particles reaching the apparatus, but the number of these particles and, more precisely, the number of particles coming from a given direction. For this it is sufficient to move, not an ionization chamber, but a counter, or better still, a number of counters mounted together in coincidence, along a meridian line. One can simply place the counters vertically, for example, and thus measure the number of particles arriving within a small angle around the zenith. As we have seen, this direction is progressively forbidden to rays of increasing penetrating power in travelling from the pole towards the equator. The values of the minimum energy required to reach the earth in a vertical direction are given below as a function of the latitude (Rossi and Fermi, Lemaitre and Vallarta).

$X$	0	20	40	60	80	90°
e.V. $\times 10^{10}$	1.9	1.5	0.65	0.12	0.0017	0

It is seen that towards  $45^\circ$  and above, all the rays capable of traversing the atmosphere can reach the ground vertically. The increase in the number of vertical particles in going towards the pole will only therefore be observed between  $0^\circ$  and  $45^\circ$  at sea-level. At higher altitudes the increase would be greater and would continue longer. It is remarkable that if we chose a direction other than the vertical, say  $60^\circ$  for example, the curves would not be very different and would have their flat parts at the same mean latitude.

## § 2. EXPERIMENTS

*Path travelled.* We have compared the numbers of particles arriving vertically at different latitudes, by moving our apparatus from latitude  $45^{\circ}$  N. to latitude  $38^{\circ}$  S. and back again, along the route Le Havre to Buenos Aires. La Compagnie des Chargeurs Réunis had given us permission to install our laboratory in an upper cabin on the "Kerguelen," and the instruments remained fixed and working during the whole of the outward and return voyages. The temperature was maintained almost exactly at  $30^{\circ}$  C., the apparatus being kept at a slightly higher temperature, and the air kept dry with calcium chloride when passing through humid regions. Objects situated above the counters only caused a very slight degree of absorption, maybe about 1.5 cm. of iron.

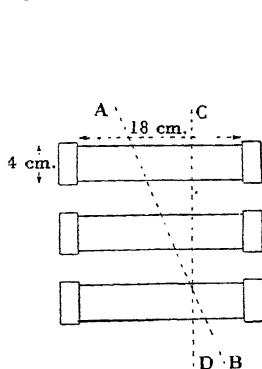


Figure 1. Position of the counters in apparatus no. 1.

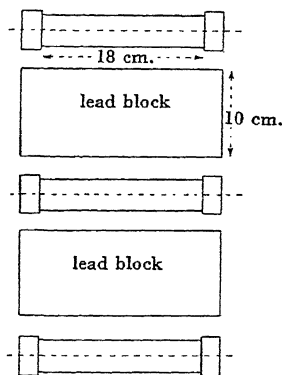


Figure 2. Arrangement of counters in apparatus nos. 2 and 3. The lead blocks are movable.

*The apparatus.* We constructed three metal cases for the voyage, each containing an outfit for detecting penetrating corpuscular rays by means of coincidences between the discharges of three Geiger-Müller counters. The scheme of the amplifier-selector followed the type described by Rossi. The impulses worked on the one hand an oscillograph, in order to permit of checking the amplitudes and the number of readings, and on the other hand a telephone totalizing relay (through the medium of a thyatron).

The counters, three in number for each outfit, were placed side by side with axes parallel, in a rotatable box. In one of the outfits (no. 1) they were placed close together (figure 1) in such a manner as to give a large number of impulses, but due to rays included in a large solid angle; vertically we obtained about a hundred impulses per hour. In apparatus nos. 2 and 3 (figure 2) the counters were sufficiently far apart to enable two blocks of lead to be placed between them, together forming a screen 20 cm. thick. These two pieces of apparatus were of identical design and their readings were alike. About twenty impulses an hour were obtained vertically.

*The counters.* The electron counters were made of iron tubes having an internal diameter of 40 mm., a thickness of 1 mm. and a useful length of 16 cm. The axial wire—which was of steel oxidized by passing an electric current through it—was 0.15 mm. in diameter and was stretched between two stoppers of very good ebonite cemented with Picene. The interiors, which were thoroughly dried, were filled with argon (containing a small percentage of air) under a pressure of 6 cm. of mercury. Most of these counters which were used during the voyage are still in good working order after 18 months' use; the number of impulses which they give has, however, decreased.

The counters worked under a tension of about 1400 volts and gave a range of sensitivity of some tens of volts. Great care was taken to keep them working on about the same point of their characteristic curves by checking them several times a day. They remained at a tension of 30 V. more than that at which they start to work. Before leaving they were tested in a laboratory 12 metres below the surface of

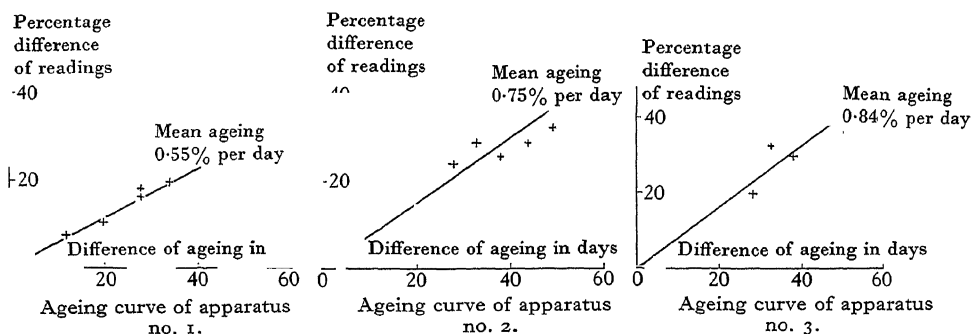


Figure 3

sandy soil, and each gave about twenty impulses a minute. The accidental coincidence of impulses among three counters separated from each other by a considerable distance (40 cm.) was about one an hour.

The counters worked in a satisfactory manner during the sixty days' voyage. Nevertheless the number of impulses given by each counter decreased regularly. It was possible to establish this effect and to correct it by comparing the values obtained on the outward and the return journeys at points on the same latitude. This ageing was linear during the voyage, the voltage being maintained absolutely uninterruptedly. The three sets of apparatus for coincidences have shown similar ageing curves (figure 3). One might perhaps attribute the phenomenon to a decrease in the active length of the wire while working. Counters which were allowed to remain inactive for a very long time have not shown this decrease.

No other correction was necessary; the barometric pressure remained very nearly constant and the movements of the ship were so slight as scarcely to increase the effective solid angle. Certain measurements were taken in more favourable conditions, for instance at Buenos Aires, Rio and Santos, where the ship remained several days.

*The principal results*

*Vertical apparatus.* If the ageing is corrected by some method, such as by taking the mean of the readings obtained at the same point going and returning, it is found that the three different apparatus indicate a decrease in the number of vertical rays as the equator is approached. This decrease is one of 16 per cent in the case of the counters which were close together, between the latitudes  $40^\circ$  (north or south) and the equator. In the case of the other apparatus it was a little less, about 13 per cent (figure 4). This result is in good agreement with those given by measurements of total ionization and with the recent measurements taken by Rossi, using counters.

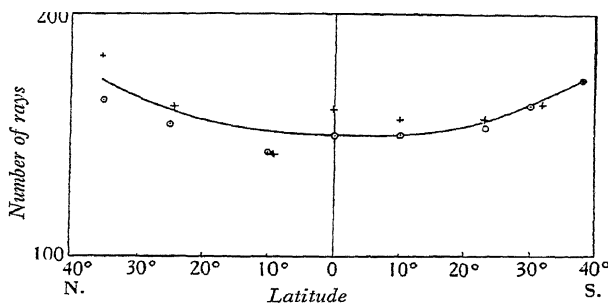


Figure 4

*Filtration.* If we now consider the effect of the 20 cm. of lead screen, we can simply compare in each case the numbers of coincidences without the screen and with the screen. The ratio of the numbers obtained in this way remained about 1.5 whatever the latitude (table I). The quality of the vertical rays did not sensibly change as regards the relative proportion of very penetrating particles, and those unable to penetrate 20 cm. of lead. The latter formed 30 per cent of the measured corpuscular radiation.

Table 1. Coefficient of absorption in 20 cm. of lead as a function of the latitude

Latitude	Mean readings during 12 hours with screens of 20 cm. of lead	Mean readings during 12 hours without screens	Ratio $\frac{N \text{ without screen}}{N \text{ with screen}}$
35° North	192	265	1.38
24° North	174	260	1.50
9° North	163	257	1.58
0°	161	260	1.62
10° South	170	235	1.38
23° South	175	235	1.35
32° South	170	260 (?)	1.53 (?)
38° South	173	240	1.40

*Rotatable apparatus.* Apparatus no. 1 was rotated through different angles with the vertical in directions east and west of the magnetic meridian. The dis-



tribution curves of the numbers of particles measured at latitude  $0^\circ$  and latitude  $38^\circ$  S. were distinctly different (figure 5). On the one hand the peak of the curve is lower at the equator, the maximum for the vertical is less than in higher latitudes,

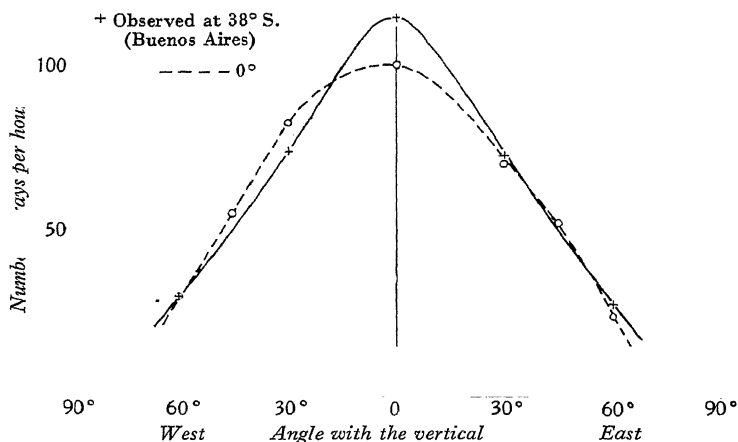


Figure 5. Number of rays as a function of their direction.

and on the other hand it is distinctly unsymmetrical, the rays at  $30^\circ$  and  $45^\circ$  W. being more numerous than those coming from the east at the same angles. This result is comparable with those obtained by Johnson, Stearn and Bennett, and Rossi.

### *Interpretation*

The curves showing the decrease in the number of particles arriving vertically are in good agreement with the theories summarized above and also with the results of experiments made with ionization chambers. The voyage was not continued sufficiently far towards the pole to enable the threshold to be observed. The constancy of the coefficient of absorption of the lead may perhaps be considered as showing that the proportion of feebly penetrating secondary rays produced in the atmosphere, compared with the primary particles, is constant. Thus the number of primary particles, the number of secondary particles (and perhaps the number of showers), as well as the total ionization, increase and decrease in the same manner. The dissymmetry of the distribution curve at low latitudes and its flattened shape tend to show that the greater part of the primary particles are positively charged, the majority of them arriving at the equator when moving from west to east and undergoing a considerable degree of absorption by reason of the great thickness of air through which they pass, this latter hindering observations of the maximum when displaced from the vertical, as would be observable at a greater height. It is noteworthy that Rossi has lately published the results of observations made under these conditions which are also very unsymmetrical and which show a much more rapid decline towards the east of the vertical than towards the west.

## SOME MEASUREMENTS OF COSMIC RADIATION AT HIGH ALTITUDES

BY P. AUGER AND L. LEPRINCE-RINGUET

Paris

*ABSTRACT.* The increase in the intensity of the individual components of cosmic radiation with increase in height has been measured by means of coincidence counters. At the high altitude (3500 m.), measurements were made in a simple shed, and also under a thickness of 4 m. of ice, this being equivalent in mass to 3500 m. of air. It was found that whilst the number of "hard" rays increases slightly in the range covered, the number of soft particles is about trebled. It appears also that the quantities—total ionization, single impulses, number of soft particles and number of showers—all vary together.

It is known that in rising from sea-level to 3500 m., the intensity of cosmic radiation increases about threefold. We decided to analyse this increase by separating the cosmic radiation into components and measuring these components at sea-level and at the laboratory of the Jungfraujoeh.

### §1. MEASURED COMPONENTS

The number of cosmic particles arriving vertically at a given place can be measured by an arrangement of counters (for example, three) in coincidence, mounted in a vertical plane. If the counters have thin walls (1 mm. of iron) they hardly stop any of the corpuscular radiation of energy higher than 10 m.e.V. By introducing lead screens of increasing thickness between the counters, we can stop the least energetic particles, thus causing a decrease in the number of particles indicated. Rossi has shown that this decrease, rapid at first, became very slow with thicknesses of lead greater than 8 cm. We can therefore assume the existence of two groups of corpuscular cosmic rays, the one, the hard group, constituted by particles which can traverse more than 10 cm. of lead and the other, the soft group, stopped by a few cm. of lead.

Last year we made numerous measurements of the relative magnitude of these two groups in various places at latitudes from 45° to 0°. The proportion of the hard group in the total radiation was always 70 per cent, and did not appear to change with latitude (to within the moderate accuracy of the experiments).

Another type of measurement is that of showers. The method utilized by Rossi and by Gilbert, that is the measurement of triple coincidences for counters placed in the form of a V with various thicknesses of lead superposed, gives the maximum

number of showers that can be obtained at a given place. This result is not absolute but can be compared with measurements obtained using vertically disposed counters.

## §2. APPARATUS

The counters were those which we used last year for the latitude effect. They were placed in the vertical apparatus in which two slabs of 10 cm. of lead could be interposed between the counters. For the showers, the counters were placed like those of Gilbert, that is to say that at least three simultaneous rays must be emitted from the lead to produce a coincidence. The coincidence-selectors are based on the principle of that of Rossi, the impulses being registered directly off the last amplifying valve by means of a sensitive clockwork relay. The whole of the apparatus, as well as the high voltage batteries, was enclosed in boxes controlled by thermostats.

## §3. METHOD OF EXPERIMENT

The measurements were made on the terrace of the International Laboratory on the Jungfrauoch, with a simple shed to cover the apparatus and to protect it from the snow. The apparatus was then carried to a hollow prepared in the glacier in such a way that the cosmic rays had to traverse 4 m. of ice before reaching the apparatus. This thickness is equivalent in density to the screen formed by the atmospheric air between 3500 m. and sea-level.

## §4. RESULTS

These can be summarized in a table where the numbers of coincidences per minute observed with different arrangements are indicated. The total number of impulses measured for each experiment is from 600 to 1000 according to circumstances.

On the terrace	{	Vertical coincidences without lead screens	1.9
		Vertical coincidences with 20 cm. of lead	1.0
		Counters in V formation without lead	0.7
		Counters in V formation with 2 cm. of lead	1.65
Under 4 m. of ice	{	Vertical coincidences without lead screens	1.1
		Vertical coincidences with 20 cm. of lead	0.76
		Counters in V formation without lead	0.55
		Counters in V formation with 2 cm. of lead	0.55

To make the results of the two series of experiments comparable, it was necessary to apply a correction to the measurements made on the terrace because the large number of impulses due to each counter brought about a diminution of the efficiency of the coincidence apparatus. This correction was made empirically by means of a small quantity of radium, by which the natural impulses in all the counters could be equalized everywhere, without influencing the true coincidences.

## § 5. REMARKS AND CONCLUSIONS

The earlier measurements made at sea-level gave the proportion of 70 per cent of hard rays as the partition coefficient between hard and soft rays. We found the same value at 3500 m. under 4 m. of ice, which implies that air screens and ice screens of the same total density are equivalent. On the other hand, at 3500 m. and in free air, the proportion of the hard rays fell to 52 per cent, whilst the total corpuscular radiation increased from 1.1 to 1.9. We can say that the number of hard particles increased slightly (0.76 to 1) in rising to 3500 m., whilst the number of soft rays was approximately trebled. This is the same increase as is shown in the simple impulses of a single counter.

Again, the shower measurements showed that at 3500 m. the maximum is reached with 2 cm. of lead, and that the value beneath 4 m. of ice with the same lead is only one-third of that value. The showers follow the soft corpuscular radiation in their variations; we may suppose that they constitute the greater part of the soft radiation.

Finally, beneath ice (and very close to it on all sides, because the working chamber in the glacier was a cube of only 8 m. side) we did not observe the great increase that was apparent on increasing the thickness of superimposed lead in free air.

## § 6. INTERPRETATION OF THE RESULTS

The experiments which we have made, together with those made by other experimenters (Rossi, Gilbert), can be interpreted simply in the following manner:

(1) There are, amongst the particles of the cosmic rays arriving in a vertical direction, two well-defined groups; one is the hard group, capable of traversing several tens of centimetres of lead, each particle having an energy of several milliards (billions) of electron-volts at least; this group is doubtless formed largely from primary electrons which have experienced the latitude effect, and is relatively slowly reduced by passing through the earth's atmosphere. The other group is soft, and nearly completely stopped by some 10 cm. of lead; it is formed of electrons which cannot be primary ones, since they have not the energy of  $4 \times 10$  e.V. necessary for a primary electron to reach the earth vertically at a latitude of  $45^\circ$  against the action of the earth's magnetic field.

The soft group increases much more rapidly than the other as we rise in the atmosphere from sea-level. We may suppose that a part of it is a secondary from a non-ionizing radiation which is less penetrating than the primary corpuscular radiation.

(2) Let us examine now how the showers vary with height in the atmosphere. The most informative method is to compare the variation of the number of showers with the variation of the corpuscular radiation. To this end it is necessary first to define showers, no simple matter. Rossi, Fünfer and Gilbert have shown the importance of the geometrical conditions. When three counters are placed in V forma-

tion we obtain a number of triple coincidences, i.e. of showers, which depends on the nature and the thickness of the metal placed above the counters. With lead, and for thicknesses of the order of 2 cm., the number of showers is a maximum. We may assume that it is always possible to obtain the same maximum under the same geometrical conditions. We can then compare the number of showers with various other magnitudes; the total ionization; the number of impulses registered in a single counter, which, it seems, is the same thing (Regener); the soft corpuscular radiation and the hard corpuscular radiation.

If we thus compare the measurements made at 3500 m. altitude and those made at sea-level, or under 4 m. of ice, we see that the whole series of quantities—total ionization, single impulses of a counter, number of non-penetrating particles and number of showers—all vary in practically the same manner. On the other hand, the number of penetrating particles varies much less rapidly, and is clearly distinct from the preceding group of quantities.

It seems, then, that we must conclude from this that the hard particles are not the only local cause, either direct or indirect, of showers. Further, the soft particles are to a great extent produced when showers occur, and they seem responsible in large measure for the individual impulses of the counters and for the total ionization. The other cause of the showers is perhaps a non-ionizing, electromagnetic radiation highly absorbable in air. It would, however, be astonishing if this radiation were entirely primary and isotropic, since the latitude variation of soft corpuscular rays does not seem to differ from that of hard corpuscular rays: new experiments would be very useful here.

Finally, the fact that in the ice grotto, lead placed above the counters in V formation had absolutely no effect, or at any rate much less effect than in free air experiments, shows that ice is a sufficiently dense medium to cause a sort of saturation in showers, a saturation that lead can only modify in very slight degree.

We have completed these experiments by employing an expansion chamber controlled by counters at the laboratory on the Jungfrauoch. The number of showers obtained is very large, and the results obtained confirm the preceding results qualitatively.

# THE ABSORPTION OF COSMIC RAYS

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*ABSTRACT.* The experimental facts obtained in the experimental study of cosmic rays are summarized: the ionization is greatest at high altitudes, and decreases at any given height as the magnetic equator is approached, but remains constant over a cap of size varying with height drawn about the N. or S. magnetic pole. At high altitudes near the equator, the radiation is more intense from the west than from the east.

The azimuthal and latitude effects can be explained as effects of the earth's magnetic field on charged particles forming the cosmic rays.

From this theory, the observed latitude at which the vertical intensity of the rays commences to vary with latitude indicates what is the energy of those electrons which have a range just equal to the thickness of the earth's atmosphere. This energy is about  $4 \times 10^9$  e.V. from which it is deduced that each particle produces about 140 ion pairs per cm. of air, and that the energy loss is about  $4 \times 10^6$  e.V. per gm./cm<sup>2</sup> of absorbing material. This is in good agreement with the experimental value for the energy loss by electrons in matter, and suggests that the primary particles may be electronic.

The only direct evidence as to the nature of the particles refers to the conditions near sea-level, where electrons and positrons of energy  $10^8$  to more than  $10^9$  e.V. are present in approximately equal amounts. It is not proved, however, whether these are primary or secondary particles.

The increase in ionization at great heights cannot be due to primary electrons, since any with the appropriate range to account for the ionization would not enter the earth's atmosphere owing to the magnetic field. The effect must therefore be due to secondary particles associated with high-energy electrons and positrons or to uncharged particles, to photons or to heavy particles.

As regards the "showers" which are produced in matter by cosmic rays, it is pointed out that the shower-producing radiation is not the primary radiation itself, but is much more absorbable than the latter; it is possible that it consists of  $\gamma$  radiation of energy  $10^9$  volts or more.

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ONE of the main difficulties which stand in the way of a satisfactory interpretation of the phenomena of the cosmic radiation lies in our ignorance of the exact mechanism of the absorption of photons and charged particles of very great energy.

In fact, it is only through the study of cosmic rays that we can hope at present to learn about the properties of very energetic radiations. But since the experimental phenomena of cosmic rays are both complicated and hardly at all under the experimenter's control, it is by no means easy to find their correct interpretation. For to do this implies the analysis of the obviously complex radiation into simpler constituents and then the decision as to the nature and properties of the various radiations.

Unfortunately we cannot get much help in this process from theoretical physics for there seems to be no theory which is certainly valid for particles and photons of very great energy. While it is quite certain that, in the cosmic radiation, we have to deal with particle energies of the order of  $10^8$  to  $10^{11}$  e.V. (electron volts), it seems nearly equally certain that the only existing theory for dealing with fast electrons and photons, that of Dirac, is only valid for energies less than  $137mc^2$ , that is about  $7 \times 10^7$  volts.

The main facts which have to be explained are the following. The ionization due to the cosmic rays amounts to about 350 J., that is 350 ion pairs per  $\text{cm}^3$  per sec., at the top of the atmosphere, and decreases downwards to 2 J. at sea-level and finally reaches about 0.01 J. at a depth underground corresponding to about 500 metres of water. The ionization at sea-level is constant, from the magnetic poles to  $50^\circ$  N. and S. magnetic latitudes, and then falls till at the magnetic equator it is about 12 per cent less. At a height of 9000 m. above the earth's surface the reduction at the equator is about 40 per cent less than at high latitudes. At sea-level in moderate latitudes the radiation is equally intense in all directions, but at high altitudes near the equator the radiation is more intense from a westerly direction. For instance, at an altitude of a few thousand metres near the equator the westerly intensity is about 16 per cent greater than the easterly intensity.

This azimuthal asymmetry and the variation of intensity with latitude receive a simple interpretation on the basis of Störmer's theory of the deflexion of charged particles by the earth's magnetic field. This theory has been applied to the case of the cosmic rays by Rossi, Lemaître and Vallarta and others. The theory is complicated, but for the present discussion it is sufficient to quote the following results. A positively charged electron coming from infinity can only reach the earth in magnetic latitude  $\lambda$ , if its energy has a certain limiting value  $V_1(\lambda)$ , and it can then only arrive from a direction due west along the earth's surface. If such a positron has a certain greater energy  $V_2(\lambda)$  it can arrive from any direction. For intermediate energies, such particles can arrive from certain directions only, comprised within a certain cone centred in the west. If the particles are negatively charged, the above argument holds if east is substituted for west.

The following convenient numerical result will be useful for the discussion. Electrons of either sign can only arrive at latitude  $\lambda$  in a direction in the meridian plane if their energy in electron volts is greater than

$$V_m = 1.9 \times 10^{10} \cos^4 \lambda \quad \dots\dots(1).$$

The observed constancy of the ionization at sea-level from the poles to a latitude about  $50^\circ$  and then the drop to the equator is simply explained by the effect of the earth's atmosphere. This prevents any particles from reaching the earth's surface which have a range less than the thickness of the atmosphere. The energy required to penetrate the atmosphere can be found by putting in (1) the observed value  $\lambda_c$ , at which the vertical intensity of the cosmic rays starts to vary with latitude. Taking this as between  $45^\circ$  and  $50^\circ$  we find for the energy for an electron to penetrate the atmosphere, a value about  $4 \times 10^9$  e.V. Since the height of the equivalent homo-

geneous atmosphere is about 8.5 km., and the energy to produce a pair of ions is about 33 volts, this result shows that each particle produces about 140 ion pairs per cm. of air. This result is in close agreement with the figure of 135 ion pairs per cm. obtained by Kolhörster and Tuwim, based on a comparison of the measured ionization with the number of discharges of a counter\*.

If we assume that the absorption of the particles is proportional to the mass of the absorber†, then the atmosphere is equivalent to about 10 m. of water. So we get an energy of about  $4 \times 10^8$  e.V. per metre of water, or  $4 \times 10^6$  e.V. per gm./cm.<sup>3</sup>

A detailed discussion of these experimental facts has been given by Johnson, who concludes not only that nearly the whole of the incident radiation must consist of charged particles, but also that the great majority of the particles must be positively charged. It is difficult to say how rigorous this conclusion is, but certainly the greater part of the primary radiation which penetrates into the lower half of the earth's atmosphere must be considered as positively charged. However, comparatively little is known of the radiation in the upper parts of the atmosphere; in particular the variation with latitude is not so well known, nor is the azimuthal distribution. So it is less possible to be certain that negatively charged particles or photons may not also be present. It may be necessary to postulate the existence in the upper atmosphere of multiply charged particles. However, Regener's new result that the intrinsic ionization does not increase at great heights makes it improbable that any great number of heavily charged particles are present.

The only direct evidence available as to the nature of the particles is that obtained by cloud photographs and these have only been obtained near sea-level. The results show that almost all the ionization at sea-level is due to about equal numbers of electrons and positrons with energies from  $10^8$  to over  $10^9$  volts. But it is probable that many if not most of these particles are of secondary origin, being most likely produced by "showers" in the atmosphere.

A few particles are observed in the cloud photographs with curvatures in a magnetic field indicating energies up to  $10^{10}$  e.V. These also may well be positrons and electrons but there is the possibility that some of them may be protons. For there are fairly strong theoretical reasons for believing that protons of such energies produce tracks so little different from electron tracks, as regards ionization density, that the existing measurements would have failed to distinguish them. Thus the existing evidence is not sufficient to allow a definite decision as to whether the *primary* radiation at sea-level consists of particles of electronic or protonic mass. The photographs do, however, make it fairly certain that, *at-sea level*, there are no appreciable numbers either of primary photons or particles with more than a single electronic charge.

Some less direct evidence as to the nature of the particles can be obtained from the analysis of the variation of ionization with depth below the top of the atmosphere.

In the first place it is not possible to attribute the main part of the great increase of ionization at high altitudes to the stopping of primaries of electronic mass. For

\* Regener recently has obtained a value as low as 103 ion pairs per cm. of path.

† This has been verified approximately for the primary cosmic radiation at sea-level.



electrons, which have a low enough energy to be stopped by a layer of atmosphere equivalent to one or two metres of water, would have an energy less than the critical energy given by (1), that is they could never reach the top of the atmosphere at all except in very high latitudes, as they would be deflected away by the earth's magnetic field. Thus the ionization high up in the atmosphere must be due to secondaries of some kind, or to uncharged particles or photons, or to charged particles with a smaller range than electrons of the same magnetic deflectibility, for instance  $\alpha$ -particles or particles with still larger charges.

About halfway up the atmosphere, a slight but quite definite hump has been found by Piccard and Cosyns, and by Compton, in the curve of ionization against height. This must certainly be interpreted as due to a fairly homogeneous group of particles with a range of about 5 m. of water. It is difficult to be certain of their nature. It is just possible perhaps to identify them with particles of electronic mass, but their range is already rather smaller than we should expect for the lowest energy electrons which are allowed by Störmer's theory to reach the earth in moderate latitudes. If further experiments show that this hump still exists in higher latitudes, say at  $60^\circ$ , then it will definitely be necessary to attribute it not to electrons, but to more highly charged, or heavier, particles.

The experiments under water and in deep mines have revealed two maxima of the ionization, one at 250 m. of water found by Clay in the Red Sea, and one at an equivalent depth of 500 m. of water found by Corlin in Sweden. These maxima must be attributed to the presence of two fairly homogeneous groups of particles. If they are electrons their energies will be about  $10^{11}$  and  $2 \times 10^{11}$  e.V., if we assume the same energy loss of  $4 \times 10^6$  e.V. per cm. of water.

The only direct measurements of the energy loss of fast electrons in traversing matter are those of Anderson on cloud photographs, showing tracks passing through lead plates. Anderson finds that electrons and positrons of energy about  $300 \times 10^6$  e.V. lose energy at the rate of about  $57 \times 10^6$  e.V. per cm. of lead, that is at the rate of about  $4.3 \times 10^6$  e.V. per gm./cm.<sup>2</sup> of absorber. The fact that this value for electrons and positrons is in close agreement with the value of  $4 \times 10^6$  e.V., found by the two quite different methods already mentioned, makes it plausible to assume that the primary radiation reaching the earth's surface may consist of particles of electronic mass. However, this argument cannot exclude the possibility of protons being present, as the ionization by protons of very high energy may well be very similar to that of electrons.

An independent confirmation of the correctness, as regards order of magnitude, of Anderson's value of  $57 \times 10^6$  e.V. per cm. of lead can be obtained by comparing the energy spectrum of the particles as observed by Anderson and by Kunze by the cloud chamber method, with the absorption of the particles as observed by Rossi with counters. For the latter measurements can only be interpreted as giving an energy spectrum consistent with the former, if an energy loss of this order is assumed.

When we try to explain the average ionization of about 140 ion pairs per cm. of air, we must consider three processes.

(a) The loss of energy in distant collisions with the orbital electron of the molecules of the absorber, giving rise to excitation and ionization.

By relying on the few direct ion counts made on cloud photographs, it seems probable that these processes cannot account for much more than 50 ion pairs per cm.

(b) The loss of energy by such close collisions of the primary particle with the orbital electrons as give rise to secondaries of considerable energy. The classical theory given by Heisenberg gives a value of about 20 ion pairs per cm. for this form of absorption.

Very little direct experimental evidence of the frequency of these secondary tracks has been obtained, but what there is, is at any rate not in conflict with the above theoretical estimate.

(c) The third process of absorption known is through the production of showers. Since the first two processes give together 70 ion pairs per cm., whereas the observed total is 135 ion pairs per cm., the production of showers must be supposed to account for the remaining 65 ion pairs per cm.\*

Very little is yet known about the mechanism of the production of showers. But the photographs of showers obtained with cloud chambers, together with their investigation by the use of several counters, has led to the following results. The showers consist of the simultaneous projection of numbers of particles, mainly positrons and electrons. As many as 80 such tracks have been observed by Anderson on one photograph, but showers of 10 to 20 tracks are much more common. The energies of the individual particles vary from a few million to several hundred million volts, while the total energy of all the particles in a large shower may amount to about  $3 \times 10^9$  e.V. Many showers are very complicated, with particles going in all directions, but others show a fairly simple structure and consist often of a group of tracks diverging usually downward from some point or small region in the material surrounding the chamber.

The showers are not mainly produced directly by the primary corpuscular radiation, but by a secondary and probably non-ionizing radiation produced by the primary rays. This secondary radiation, which we may call the shower-producing radiation, is very much more rapidly absorbed than the primary radiation, and its absorption coefficient increases rapidly with the atomic number of the absorber. In fact the absorption coefficient of the shower-producing radiation varies roughly as  $Z^2$ , where  $Z$  is the atomic number of the absorber. This result is in striking contrast to the case of the absorption of the primary rays. For these the mass-absorption law holds roughly, that is the absorption coefficient varies approximately as  $Z$ . In heavy elements the penetrating power of the secondary shower-producing radiation is much less than that of the primary corpuscular radiation.

Since the particles produced by the shower-producing radiation seems to consist mainly of about equal numbers of positrons and electrons, and since hard

\* If Regener's new and lower value of the specific ionization be accepted, then the amount of energy lost in shower formation will be smaller than that estimated above.

$\gamma$ -rays are known to be absorbed mainly by the production of positron-electron pairs, it is plausible to identify the shower-producing radiation with photons of high energy. It is significant that the absorption coefficient of gamma rays of 2 to 5 million volts energy is numerically nearly the same and varies in the same way with the atomic number of the absorber as does the shower-producing radiation. We must remember, of course, that the shower-producing radiation, if it consists of photons, as is suggested here, must consist of photons of great energy, up to  $10^9$  volts. So the comparison mentioned above suggests that photons of very great energy have about the same penetrating power as photons of a few million volts. However, this conclusion cannot be said to rest on very certain foundations.

It has been estimated above that the primary particles lose, on the average, about half their energy in ionization and the production of single secondaries, and about half in shower formation. Now this conclusion can be checked roughly by observing with counters the absolute number of showers produced in an absorber by the incident rays. No accurate figures are available, but the results obtained are not inconsistent with their estimate of the amount of energy lost by shower formation.

We can thus form the following picture of the absorption of the primary cosmic ray particles by shower formation.

A primary particle of  $10^9$  to  $10^{10}$  e.V. energy can make collisions, probably with atomic nuclei, in which a number of photons of high energy are emitted, mainly in the forward direction. The effective cross-section  $\sigma$ , for this process, which can be considered as the emission of a type of collision radiation, varies roughly as the nuclear dimensions ( $\sigma \propto Z$ , if the mass-absorption law holds).

The actual value of the cross-section is probably of the order of a few per cent of the nuclear area.

The second stage in shower formation is the absorption of the secondary photons, mainly by the production of single and multiple positron-electron pairs. The cross-section for this process varies roughly as  $Z^2$ , and for heavy elements, that is for large  $Z$ , is several times larger than the nuclear area.

This scheme is, of course, far too simple, and is intended only to give a plausible first outline of these extraordinarily complex phenomena.

As regards the nature of the primary particles which produce the shower-producing radiation\*, the most likely possibilities, except perhaps in the upper atmosphere, are singly charged particles of electronic or protonic mass.

If Johnson's analysis is valid and the incident radiation is all positively charged, then it must consist of positrons or protons. Since slow proton tracks are rare in the cloud chamber, it seems more plausible to assume the former. There is certainly no direct evidence of the presence of many fast protons in the cosmic radiation, but there is no definite evidence that none are there.

It should be possible to distinguish between electron tracks and proton tracks of very great energy by measuring the ionization along the tracks. For theory

\* Showers can almost certainly also be produced by energetic electrons having their origin in other showers higher up in the atmosphere.

suggests that the ionization along a very fast proton track should be about 30 per cent less than along an electron track with the same curvature. However, sufficiently accurate ion counts have not been made to test the theory.

There is some indirect evidence that protons may be present from considerations of the variation of ionization with depth. If we attribute the main part of the ionization in the lower part of the atmosphere to electrons and positrons, then we might attribute the very penetrating rays which can penetrate 500 m. of water to protons. For theory suggests that a proton, owing to its greater mass, is likely to be much less absorbed by processes involving the emission of radiation and by the production of secondaries.

# A VERY HIGH ALTITUDE SURVEY OF THE EFFECT OF LATITUDE UPON COSMIC-RAY INTENSITIES AND AN ATTEMPT AT A GENERAL INTERPRETATION OF COSMIC-RAY PHENOMENA

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**ABSTRACT.** The results of a very high altitude geographical survey extending from Northern Canada to Peru, carried out in airplanes at altitudes up to 22,000 ft., and in three stratosphere flights made within the United States to altitudes of 60,000 ft., are interpreted in the light of (1) the Epstein and the Lemaitre-Vallarta analysis of the effect of the earth's magnetic field, and (2) the Bowen-Millikan proof that the immediate agents responsible for the ionization of the atmosphere are electrons (+ and -), rather than protons or heavier nuclei.

The main conclusions reached are:

(1) that the resistance of the atmosphere to incoming electrons is  $10^9$  e.V. on account of the primary ion-track and  $5 \times 10^9$  e.V. on account of nuclear and close extranuclear encounters;

(2) that nuclear electron encounters produce only very soft secondaries, both photons and electrons;

(3) that incoming photons produce most of the ionization found at sea-level or at sub-sea-level depths;

(4) that nearly all of the non-field sensitive part of the ionization of the atmosphere above sea-level is due to photons of energy less than  $5 \times 10^8$  e.V.;

(5) that in the equatorial belt a small part of the ionization is due to incoming secondary electrons of energies as high as  $10^{10}$  e.V.;

(6) that these are responsible for the east-west effect and for the longitude effect found in the equatorial belt;

(7) that the field sensitive part of the ionization increases rapidly with increasing latitude in going from Panama to Spokane because incoming secondaries of energies decreasing from  $8 \times 10^9$  to  $2 \times 10^9$  e.V. get through the blocking effect of the field in rapidly increasing numbers with increasing latitude and add greatly in northern latitudes to the underlying ionization of the upper air produced by the incoming photons;

(8) that the only source of the observed cosmic-ray energies now in sight is matter-annihilation;

(9) that the softest components of the cosmic rays have the energies corresponding to the partial annihilation or atom-building hypothesis, while the hardest components have energies corresponding to the complete atom-annihilation hypothesis;

(10) that these processes may conceivably be taking place (1) because of the very low temperature that facilitates the clustering of hydrogen in interstellar space, or (2) because of such extreme temperature conditions of the opposite sort as are found in novae, as suggested by Baade and Zwicky.

## § 1. INTRODUCTORY

THE following is a detailed report of the results of a very high altitude survey of the effect of latitude upon cosmic-ray intensities planned in the late fall of 1931, a preliminary report upon which was made at the Atlantic City meeting of the Am. Ass. Adv. Sci. in December, 1932\*†. As indicated in that report, as well as in a lecture‡ delivered in Paris in November, 1931, such latitude effects were to be anticipated at high altitudes, even if they did not appear at low. For cosmic-ray photons traversing space in all directions must in any case produce secondary electrons wherever they traverse matter, whether that be in interstellar space, in nebulae, or in the atmospheres of suns through which they must sometimes pass in their travel of billions of years through space. So that if cosmic ray photons exist at all, space must be traversed in all directions to some extent, at least, both by these photons and by their secondary electrons. The only question for experiment to determine is as to the proportions between the two.

It was thought that a suitable high-altitude survey would throw light upon this question. For these electronic secondaries were expected, from the direct cosmic-ray energy measurements already under way at the Norman Bridge Laboratory and from Epstein's calculations published as early as 1930, to possess energy insufficient to penetrate to the earth's surface at the equator through the blocking effect of the earth's magnetic field, but amply sufficient to penetrate that field in the higher magnetic latitudes. To be specific, Epstein§ had found that  $10^9$  e.V. electrons could only penetrate north of magnetic latitude  $59^\circ$ . Since, however, such latitude effects had been shown to be non-existent at the earth's surface in the region between Pasadena (mag. lat.  $41^\circ$ ) and Churchill, Manitoba|| (mag. lat.  $70^\circ$ ), it was thought highly important from the standpoint of our planning in 1931 to look for them at high altitudes in northern Canada, where electrons of too low energy to penetrate to sea-level might get through the earth's magnetic field and make their presence felt in the upper regions of the atmosphere.

Indeed, Epstein's analysis had shown that electrons of a given energy *should be distributed uniformly over a polar cap* which should of course extend farther and farther south the higher the incoming energy. In this analysis, however, atmospheric absorption had been ignored. But the greater part of the electrons the energies of which were being directly measured in the Norman Bridge Laboratory actually had energies under  $10^9$  e.V., and since no appreciable number of  $10^9$  e.V. electrons could possibly penetrate the atmosphere (see below), even if they could get through the earth's magnetic field, it is obviously only at high altitudes that the effects of such entering electrons could be expected to be observed. Epstein's figures were

\* R. A. Millikan, *Phys. Rev.* **43**, 665 (1933).

† Bowen, Millikan and Neher, *Phys. Rev.* **44**, 246 (1933).

‡ R. A. Millikan, *Annales de l'Institut H. Poincaré*, 1933, p. 452.

§ Paul S. Epstein, *Proc. Nat. Acad. Sci.* **16**, 658 (1930).

|| R. A. Millikan, *Phys. Rev.* **36**, 1597 (1930). These results were checked in 1932 by Millikan and Neher (between Pasadena and Victoria, B.C.) and by Bennett, Dunham, Bramhall and Allen, *Phys. Rev.* **42**, 446 (1932).

available to us when we planned this high altitude survey in the late fall of 1931. We therefore arranged at that time, through the kind assistance of the Royal Canadian Air Force, to make our northernmost high altitude airplane flight at Cormorant Lake, Manitoba in magnetic latitude  $63^{\circ}$  N., where we hoped to get a crucial test of the existence inside this cap of incoming electrons of energies  $10^9$  e.V. or less. The other localities in which we planned and carried out flights in the succeeding summer (1932) were Spokane ( $54^{\circ}$  N.), where Captain Breene flew most skilfully for us; March Field, California ( $41^{\circ}$  N.), where Col. Arnold and the other officers of the Field were extraordinarily generous in their assistance; Panama ( $20^{\circ}$  N.), where Gen. Foulouis gave directions again for Army assistance; and Peru ( $4^{\circ}$  S.), where the Pan-American Airways pilots flew to high altitudes for us. The success of these airplane observations is largely due to the development of a vibration-free electroscope yielding as good photographic records on a moving and tipping platform, such as that of an airplane, as in a laboratory.

## § 2. THE RESULTS OF THE 1932 AIRPLANE LATITUDE SURVEY

The whole of the results of the aforementioned survey are given in figure 1, in which the readings at different depths, in metres of water, beneath the top of the atmosphere, are reduced to ions per  $\text{cm}^3$  per sec., formed in air at atmospheric pressure. The geomagnetic latitude is determined from the assumption generally made now by geophysicists that the chief component of the earth's magnetic field is a dipole, the northern pole of which is situated at  $69^{\circ}$  W.,  $78^{\circ} 30'$  N.

The main points to be noted in connexion with figure 1 are (1) that up to the altitude reached, namely 4.5 m. of water beneath the top, no detectable difference is found between the readings at Cormorant Lake ( $63^{\circ}$  N.) and those at Spokane ( $54^{\circ}$  N.); (2) that at 4.5 m. (alt. 22,000 ft.) there is a 12 per cent larger ionization at Cormorant Lake and Spokane than at March Field, and that this difference decreases smoothly to zero at sea-level; (3) that no measurable difference appears between the curves taken in Panama ( $20^{\circ}$  N.) and Peru ( $4^{\circ}$  S.); (4) that at 22,000 ft. the Panama reading at  $20^{\circ}$  N. is 29 per cent lower than the March Field reading and 38 per cent lower than the Spokane and Cormorant Lake readings; (5) that the area between the uppermost and the lowermost curves represents that portion of the ionization which is due directly or indirectly to field-sensitive rays, while the area underneath the lower curve is that portion of the ionization which is due to non-field sensitive rays.

## § 3. LOSS OF ENERGY OF INCOMING COSMIC-RAY ELECTRONS IN REACHING SEA-LEVEL ABOUT $6 \times 10^9$ e.V.

Anderson and Neddermeyer have counted with a great deal of care the average number of ions formed per centimetre by a high speed cosmic-ray electron at normal pressure. This can be done accurately if cloud chamber tracks are chosen which correspond to the passage of an electron a little before the expansion so that the ions have had, say, a second to diffuse before the water condenses upon them, for

the droplets are then well separated. The result obtained from these measurements is 31 ions per cm. According to Kulenkampff's measurements, each electron removed from the molecules of air represents an expenditure of 32 e.V. of energy. These figures give 990 e.V. of energy lost per cm. of air-path. This, multiplied by the number of centimetres of air in an atmosphere, namely,  $1033/0.00117 = 8.83 \times 10^5$ , gives  $8.7 \times 10^8$  e.V. loss of energy in penetrating the atmosphere. Since the greater part of the electrons that reach the earth's surface have come in within  $45^\circ$  of the normal, we may take the average electron as entering at say  $30^\circ$ , the cosine of which is 0.86, so that  $10^9$  e.V. per atmosphere may be taken as the energy dissipated per electron in reaching the surface *on the incorrect assumption that no secondary rays of any kind are formed between the top of the atmosphere and sea-level.*

There are, however, three different ways of determining the *total* resistance of the atmosphere, *including the formation of such secondaries.*

(1) According to Epstein's computations, which are in excellent agreement with those of Lemaitre and Vallarta\*,  $2.4 \times 10^9$  e.V. rays will just begin to get through the earth's magnetic field at magnetic latitude  $49^\circ$ , and be completely through at latitude  $57^\circ$ , so that there should be a latitude effect due to these rays, as well as to those of lesser energy, between Spokane (mag. lat.  $54^\circ$ , where  $2.4 \times 10^9$  e.V. rays should be varying most rapidly), and Cormorant Lake, provided incoming or extra-terrestrial secondary electrons of these energies exist at all. Anderson's direct energy measurements at sea-level have revealed the existence of such rays, of from 2 to  $4 \times 10^9$  e.V. formed in the material about the cloud chamber and they should, of course, also be formed when the primary rays traverse matter outside our atmosphere; in addition, the high altitude latitude effect found farther south (figure 1) shows that even higher energy electron rays do come into the atmosphere from outside, else there could be no high altitude latitude effect. *The reason, then, that we did not find a latitude effect between Spokane and Cormorant Lake must be that rays of the energy of  $2.4 \times 10^9$  e.V. cannot penetrate the atmosphere so as to show their effect at the highest altitude at which we make measurements, namely, 4.5 equivalent metres of water beneath the top of the atmosphere.* This means that the total resistance of the atmosphere (equivalent to 10 m. of water) to incoming electrons (+ or -) must be more than  $\frac{10}{4.5} \times 2.4$ , or  $5.3 \times 10^9$  e.V. A possible uncertainty in this mode of approach to the problem lies in the fact that we cannot have complete assurance that locating the effective position of the North magnetic pole for the purposes here under consideration at  $79^\circ$  N.,  $68^\circ$  W., is strictly legitimate, though it is the recognized practice of geophysicists, and, in addition, *it introduces a larger measure of self-consistency into our own geographical readings than does any other point when used as a magnetic pole.*

(2) The second mode of approach is to start with Anderson and Neddermeyer's direct measurements of the loss in energy of electrons of energy between 40 million and 300 million e.V. in passing through lead. The mean value of this energy-loss (see the paper by Anderson and Neddermeyer on page 171) is now 57 million e.V.

\* Lemaitre and Vallarta, *Phys. Rev.* 43, 91 (1933).



per cm. of lead. Since the mass absorption law holds fairly well in the highest energy range in which the loss of energy of electrons in traversing matter has been measured, lead having in fact some 9 times the absorptive power of water\* per cm.<sup>3</sup>, we shall assume that this relation holds for cosmic-ray electrons. We then obtain for the resistance of the atmosphere (10 m. water) a figure of  $57 \times 10^6 \times \frac{1033}{9} = 6.5 \times 10^9$  e.V. This might be in error by 20 per cent, but probably not more.

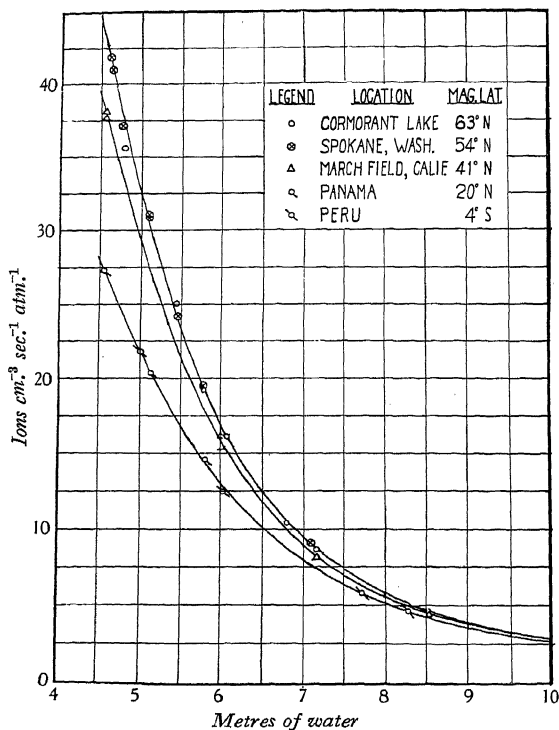


Figure 1.

(3) The third mode of approach is to utilize the fact that there is no sea-level latitude effect between Pasadena (41° N.) and Churchill (69° N.), while there is a marked latitude effect higher up in the atmosphere (figure 1). But according to Epstein it takes just  $4 \times 10^9$  e.V. to begin to get through the earth's magnetic field at 40° N., and these electrons will produce a latitude effect up to mag. lat. 52°. A marked latitude effect is actually shown in the upper air (figure 1) in this region, but none at sea-level. Hence, if there are  $4 \times 10^9$  e.V. incoming or extraterrestrial secondaries, the resistance of the atmosphere must be at least  $4 \times 10^9$  e.V. to prevent them from reaching sea-level. Indeed, a few 6, 7 and even  $8 \times 10^9$  e.V. are needed to produce the latitude effect shown in figure 1 between Panama (20° N.) and Pasadena (41° N.).

\* See *Radiations, etc.*, Rutherford *et al.*, p. 427, 1930; also Bethe; *Z. f. Physik.* 76, 293 (1932).

Again, according to Epstein and Lemaitre, the latitude effect for energies of  $5.5 \times 10^9$  e.V. should begin at lat.  $34^\circ$  and be finished at lat.  $50^\circ$ . *Its practical absence at sea-level means that the resistance of the atmosphere is at least that much.* The effect of the few 7 and  $8 \times 10^9$  e.V. needed to explain the observed latitude effect both in high altitudes and at sea-level down to lat.  $20^\circ$  would be finished at about  $45^\circ$  and should be very small down to  $41^\circ$ , so that the practical absence of a sea-level effect between  $41^\circ$  and the pole fixes the total resistance of the atmosphere at about  $6 \times 10^9$  e.V. In view of the three modes of approach, especially the last two, this value can scarcely be in error by as much as 20 per cent.

The main result of this whole analysis of atmospheric resistance to incoming electrons is found in the conclusion that *about five-sixths, or 83 per cent, of all the "field-sensitive" ionization found between the upper and lower curves of figure 1 is due to secondaries formed within the atmosphere.*

A second result of nearly equal importance is that, since none of these secondaries, either photons or electrons, is sufficiently penetrating to reach sea-level and reflect there the latitude effects actually existing at higher altitudes, they are on the average low energy secondaries, the photons probably having an average energy, estimated from their inability to reach sea-level, of less than say 50 million e.V., while the secondary electrons must for the same reason have an energy under, say,  $5 \times 10^8$  e.V. This checks qualitatively with the results already published, for the energies of these very photons are exhibited in figures 7, 8, and 10, pp. 358-9, *Phys. Rev.* **45**, and those shown all have energies under 30 million e.V. and many of them under a million. In fact, the energy of the photons produced by the disappearance of positive electrons, such as are always formed in high energy nuclear encounters, is known from the experiments of Chao\*, Gray and Tarrant†, Thibaud‡, and Lauritsen§, to be about 0.5 million e.V., and many such must be formed. Also, the electron secondaries formed by electrons, examples of which are shown in figures 13 and 14, p. 361, *Phys. Rev.* **45**, are in these particular cases seen to possess energies only up to 50 million e.V. Indeed, not only Anderson's and Neddermeyer's photographs, but all  $\beta$ -ray photographs, show that the transfer of a very large part of the energy of an electron to another electron is a very rare event, while a high energy photon in general transfers a large fraction of its energy to the electron with which it collides.

#### §4. SECOND PROOF OF THE ATMOSPHERIC ORIGIN OF THE GREAT BULK OF THE OBSERVED IONIZING COSMIC-RAY PARTICLES

A preliminary report was made at Atlantic City in December 1932 upon the results of a second method of testing whether or not a very large fraction of the ionization of the atmosphere is due to secondary electrons formed within our atmo-

\* Chao, *Phys. Rev.* **36**, 1519 (1930).

† Gray and Tarrant, *Proc. R.S. A*, **136**, 662 (1932).

‡ J. Thibaud, *Phys. Rev.* **45**, 781 (1934).

§ H. R. Crane and C. C. Lauritsen, *Phys. Rev.* **45**, 430 (1934).

sphere. The method consists in taking an unshielded electroscopes to a very high altitude and then observing the ionization found inside the same electroscopes when it is taken to the same altitude inside a heavy shield of lead.

Figure 2 shows the results of such tests made at March Field through the cooperation of the Army officers stationed there. If the lead screen, here 10 cm. thick, acted simply as a resistance of the type considered in the first paragraph of §3, so that no secondary rays, photons, or electrons were stimulated within it, then the ratio between the ionization found in the electroscopes, first without the screen, and

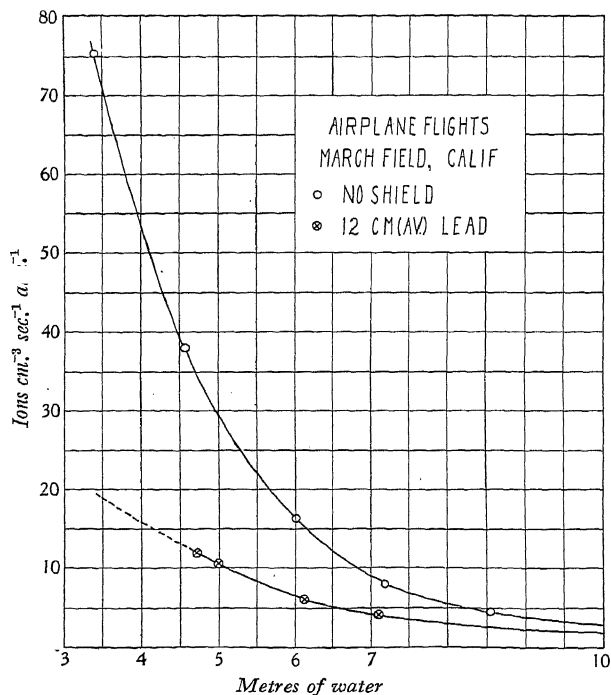


Figure 2.

then with the screen, would reveal what fraction of the electrons existing at the given altitude possess sufficient energy to penetrate the given thickness of lead. Since it is known that many new secondaries are actually stimulated within the lead, and since these all increase the actual ionization existing within the shielded electroscopes, the foregoing ratio gives merely the lower limit to the fraction of electrons having energies under the value required to penetrate the lead. Since the shield was here 10 cm. thick, the figure shows that at 29,000 feet at least 70 per cent, and probably as many as 90 per cent, of all the electron-rays existing at that altitude have energies under 570 million e.V., this being, according to the Anderson measurements, the energy required to traverse 10 cm. of lead. *Practically none of these*

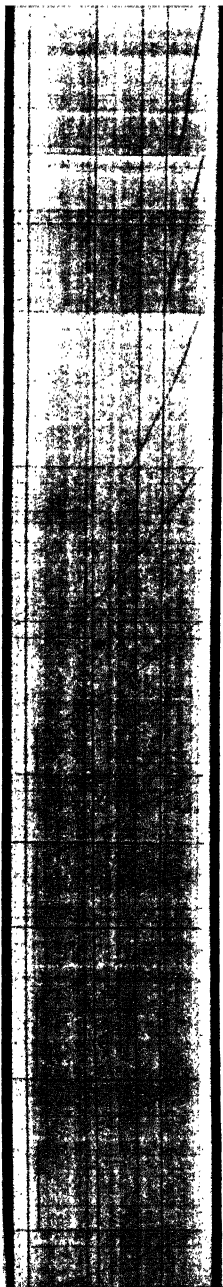
*electron-rays could have come in from outside, since it requires at this latitude at least  $4 \times 10^9$  e.V. to get into the atmosphere through the blocking effect of the earth's magnetic field, and the loss in getting down to this level is but  $2 \times 10^9$  e.V.*

#### §5. THE FORDNEY-SETTLE FLIGHT

The recent Fordney-Settle flight was even better adapted for bringing to light the cogency of the foregoing mode of approach to the problem of the origin of the ionization of the atmosphere. We had one of our self-recording instruments on that flight. Figure 3 gives a section of the film. The electroscope was automatically charged up at five-minute intervals and the slope of the line running diagonally across each interval gives the rate of discharge. The balloonists rose from 20,000 ft. to the top very rapidly—in some 20 minutes, as the record shows—and remained there for three and a half hours, then descended rapidly. The result is that the mean readings at and near the top, 62,000 feet, are very reliable, but the intervening points are less so on account of the rapidity of the ascent. The results are plotted in figure 4, the lower curve giving the results obtained by Dr A. H. Compton\* with his electroscope inside 6.0 cm. of lead. Figure 5 gives the lower limit to the fraction of the electron-rays existing at each altitude, the energies of which lie under 340 million e.V. It is seen, then, that from a depth beneath the top of the atmosphere of about 6 m. of water, i.e. from Pike's Peak up to a point but 60 cm. of water beneath the top, not less than 70 per cent, and probably less than 90 per cent, of the electron rays have

\* A. H. Compton and R. J. Stephenson, *Phys. Rev.* 45, 441 (1934).

Figure 3. Section of film from the Neher automatic recording electroscope taken during the ascent to the stratosphere in the Fordney-Settle flight of November 20, 1933. Each of the nine panels across which the sloping dark line moves from left to right corresponds to a five-minute time interval. The slope is proportional to the rate of discharge of the electroscope, which in turn is proportional to the intensity of the cosmic rays. In the first panel the balloon was at an elevation of about 20,000 feet and in the next twenty minutes (four panels), while the balloon was rising to a height of 45,000 feet, the slope, or cosmic-ray intensity, rose tenfold. From there on to the highest altitude attained, 62,000 feet, the rate of rise of the balloon was much less rapid. It remained at or near the top for three and a half hours, so that this film yielded accurate measurements of cosmic-ray intensities at the higher and lower altitudes, but not at the intermediate ones.



energies too small to penetrate the 6 cm. lead shield, i.e., they have energies under 340 million e.V. Since these figures apply to the whole atmosphere, i.e., to both the

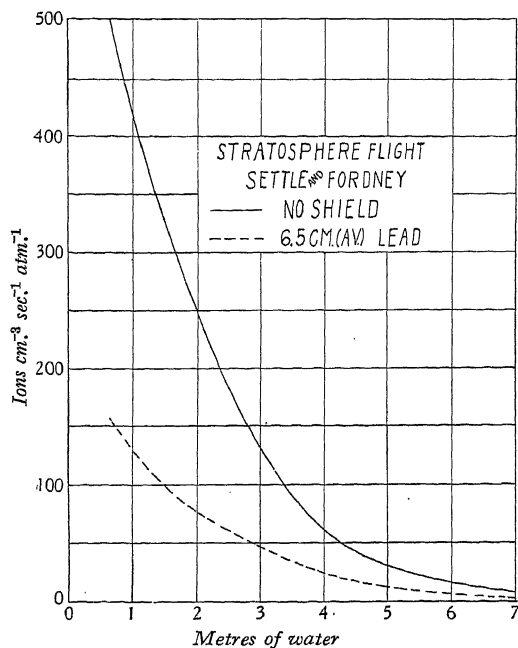


Figure 4.

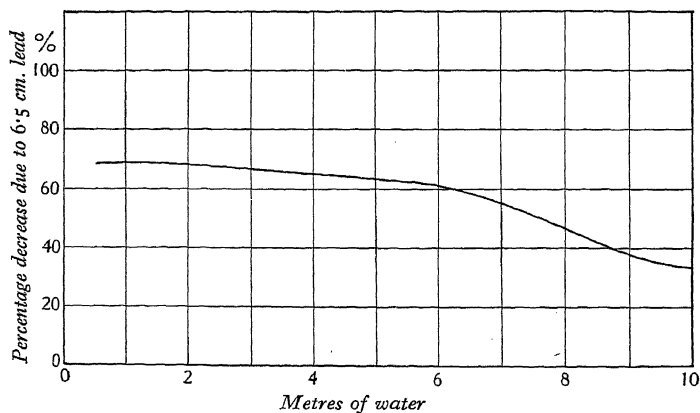


Figure 5.

field-sensitive and the non-field-sensitive parts of the ionization, we may conclude with certainty that as was stated in the Atlantic City paper in 1932, "all but a small part of the ionization of the air is due to secondaries produced within the atmosphere."

## §6. NATURE OF THE NON-FIELD SENSITIVE INCOMING RAYS

As a result of four different trips by our sensitive, self-registering, vibration-free electroscopes between Los Angeles and Mollendo, or other points on the west coast of South America, all of which yielded results in close agreement, we find that the sea-level equatorial dip in cosmic-ray intensity in this part of the world is  $7 \pm 1$  per cent. In other words, 92 per cent of the sea-level ionization here is due to non-field sensitive rays, and only  $\frac{1}{8}$  of the remaining 7 or 8 per cent is due *directly* to incoming electrons, the other  $\frac{7}{8}$  being due to secondaries produced within the atmosphere by these incoming electrons, all of which in order to get down to sea-level and produce the observed sea-level latitude effect must, according to the preceding computations, have an energy between 6 and  $8 \times 10^9$  e.V. *There need then be only enough incoming electrons of this energy to produce directly at sea-level about 1 or 2 per cent of the observed ionization.*

The 92 per cent of non-field sensitive ionization must be due either to photons or else to incoming electrons of energies somewhat above  $9 \times 10^9$ , or possibly  $10^{10}$  e.V., so that they can get through the earth's magnetic field into the equatorial belt. We have evidence which will be presented in another paper that there are at least a small number of such incoming electrons that reach sea-level in the equatorial belt—enough to produce directly at sea-level another 1 or  $1\frac{1}{2}$  per cent of the observed sea-level ionization. *Indeed, it is just these rays multiplied sixfold in their effectiveness in exciting counters by their progeny of secondaries, which are responsible for the east-west effect observed in Peru by Johnson\* and Korff†.* The incoming electrons here in question may all be assumed to be positives either arbitrarily or (better from our point of view) because the highest energy photons, which may be assumed to have produced them at some time in their travel through space, tend to be absorbed primarily by the nuclei of atoms, and in all nuclei positive electrons, of course, predominate, while hydrogen nuclei contain no negatives at all, and hydrogen constitutes, according to Russell, 95 per cent of the universe. On the other hand, the lower energy photons will of course tend to be absorbed in all substances more by extranuclear electrons, which are all negatives, for it is these extranuclear electrons that are responsible for all the ionization described by the Klein-Nishina formula. If one prefers to assume the pair theory at these high energies he may postulate that the positively charged nucleus causes the positive electron to take on the larger part of the energy of the incident photon. In any case the earth's magnetic field separates out the incoming electrons on the basis of energy, the lower energies, primarily negatives, coming in at the poles—the very highest energies, very few in number, and coming mostly perhaps from hydrogen, being the only ones able to break through at the equator.

The foregoing facts and considerations lead, then, to the presentation of the following reasons for the view that the great bulk of the *sea-level ionization*, more

\* Thos. H. Johnson, *Phys. Rev.* **45**, 569 (1934).

† S. A. Korff, *Phys. Rev.* **46**, 75 (1934).

than 85 per cent of it, and indeed of all the non-field sensitive effects, must be attributed to photons.

(1) It is precisely the above-mentioned smallness in the required number of incoming positives that is needed to remove the contradiction heretofore existing between the demands of the east-west effect for an excess of positives at sea-level, and Anderson's direct determination\* of the general equality in the numbers of positives and negatives passing through his cloud chamber at all energies, even up to  $3 \times 10^9$  e.V. Practically all of these electrons (+ and -) observed by Anderson are secondaries formed within our atmosphere and in the materials surrounding the cloud chamber. These may all be expected to be about equally divided between positives and negatives, while the 1 to 2 per cent of ionization that must be attributed to the direct effect of incoming  $10^{10}$  e.V. positives in order to account for the 6 to 12 per cent west excess observed in Johnson's and Korff's Peru work with counters, involves an excess of positives wholly negligible in Anderson's work. This is powerful support for the view that the great bulk of the sea-level ionization must be due to photons. If it were due wholly, or even in any considerable measure, to incoming positives of  $10^{10}$  e.V. energies and more, why do these not appear in the cloud chamber measurements which are capable of measuring electron energies up to  $4 \times 10^9$  e.V., with considerable reliability, this being what is left of the energy of the  $10^{10}$  e.V. after it has penetrated to sea-level? These  $4 \times 10^9$  e.V. tracks should be present in large numbers and they should be predominantly positives, quite contrary to the observations both of Anderson and of Kunze.

(2) On the other hand, photons of this order of energy are actually and unquestionably found in photographs such as figure 9 and figure 11, pp. 359 and 360, *Phys. Rev.*, **45**. Here showers are seen to spring directly from the body of the lead that can be due only to photons, since no ionizing track enters the top of the lead. Further, the joint energy of these showers is here from 1 to  $3 \times 10^9$  e.V., i.e., much too large to permit the responsible photons from being accounted for as secondaries produced within the atmosphere by incoming electrons (see § 3). There seems to be no escape, then, from regarding these showers as resulting from incoming photons themselves.

(3) If the great bulk of the non-field sensitive part of the ionization of the atmosphere is not due to these incoming photons, but rather to incoming electrons, then these latter, in order to ionize as strongly near the equator as near the poles—this is the definition of non-field sensitive rays—must possess incoming energies of  $10^{10}$  e.V. or more, and produce directly one-sixth of all the ionization found at sea-level. The other five-sixths of the ionization which these rays produce directly or indirectly at sea-level would be due to the *very low energy* secondaries that were found to be created in the atmosphere by incoming electrons (see § 3). In other words, the distribution of electron energies in a cloud chamber should then be: many energies below  $5 \times 10^7$  e.V., few if any between  $5 \times 10^7$  and  $4 \times 10^9$  e.V., and many above  $4 \times 10^9$ . This is a distribution completely at variance with that directly observed by both Anderson and Kunze, who find the great majority of the observed particles to have

\* Carl D. Anderson, *Phys. Rev.* **44**, 406 (1933).

energies between  $3 \times 10^8$  and  $3 \times 10^9$  e.V. These are much too energetic to be the secondaries produced by electrons, but not energetic enough to be the incoming electrons themselves. Further, though neither Anderson nor Kunze finds any very large number of electrons of  $4 \times 10^9$  e.V. or more, the one or two per cent of such rays necessary to account for the latitude effect, longitude effect, and east-west effect, are so few in number as to be easily reconcilable with their observations. *The great bulk of the sea-level ionization, then, appears to be due to the effects of incoming photons.* And the energies of these photons must be of the same order of magnitude as those of the observed electrons, three-fourths of which are under  $10^9$  e.V. and half under  $7 \times 10^8$  e.V.

(4) The photons of from  $10^9$  to  $3 \times 10^9$  e.V. energy *actually observed* in our 20,000 gauss field at the Norman Bridge Laboratory have ample penetrating power (see below) to produce all the effects observed by Millikan and Cameron and by Regener down to depths of from 100 to 300 m. of water, i.e., 10 to 30 atmospheres, whereas since the resistance of the atmosphere to an electron is  $6 \times 10^9$  e.V., incoming electrons to get down to such depths would have to have from  $6 \times 10^{10}$  to  $18 \times 10^{10}$  e.V. of energy. Such energies are out of all relation to those that have been found either in Pasadena or in Rostock; so that the ionization found in lakes by Millikan and Cameron and Regener can scarcely be due to anything but such photons as are actually observed in our cloud chamber. (See (2), p. 216.)

Incidentally, the relative penetrating power of photons and electrons of the same energy is of the order of 100 to 1 up to the highest accurately measured energies, and there is evidence that it remains of this order also for cosmic-rays of the highest observed energy. Thus, the total number of ion pairs formed per cm. of air path by electrons of energy 1,450,000 e.V. is given as 46\*, and at 32 e.V. per pair (the value 32 heretofore used is for electrons of a mean energy of  $10^9$  e.V.) this gives a maximum range to electrons of this energy of 1.1 cm. of water. But photons from RaC of this energy pass easily through as much as a metre of water before being reduced to say 1 per cent of their original intensity. Similarly, in the cosmic-ray field, if photons have 100 times the penetrating power of electrons, the foregoing  $18 \times 10^{10}$  e.V. required to drive electrons through 30 atmospheres of water is replaced by  $18 \times 10^8$  e.V. for photons. But photons of  $2 \times 10^9$  e.V. energy are in the range actually and commonly observed in the cloud chamber work at the Bridge Laboratory, so that the foregoing relative penetrating powers of 100 to 1 are at least in keeping with the above-mentioned facts.

(5) As for the characteristics of the ionization of the atmosphere *above* sea-level; these are even more difficult to reconcile with the hypothesis that the non-field sensitive portion is due in any large measure to incoming electrons, for figure 1 shows that the ionization, even in the equatorial belt, rises exponentially, or better as a sum of exponential terms†, right up to the highest point reached (4.5 m. below the top). This behaviour is characteristic of photon absorption, but not of electron absorption. Indeed, it was shown by Bowen, and independently both by Epstein and Langer,

\* *Radiations, etc.*, Rutherford *et al.*, p. 447, 1930; also Bethe, *Z. f. Physik*, 76, 293 (1932).

† Millikan, Bowen and Neher, *Phys. Rev.* 44, 250 (1933).



that any rays coming in uniformly from all directions as the cosmic-rays do, and ionizing uniformly along their path, as electrons do, when we neglect their nuclear secondaries, would give rise to a linear variation of ionization with altitude measured from the end of their range, i.e., from the level of the mean depth to which they penetrate.

Now, since the energy of all incoming electrons that can get through the blocking effect of the earth's field into the equatorial belt is  $10^{10}$  e.V. or more, the end of the range is nearly two atmospheres below the top, so that a linear rate of increase above this level represents say a 50 per cent increase from sea-level up to 22,000 ft. (4.5 m.) and a still smaller increase from 4.5 m. up to the top. *The observed increase is, on the other hand, some 1000 per cent from sea-level up to 22,000 ft., and probably much more than that above that point.*

This enormous discrepancy can be somewhat reduced, but by no means eliminated, by taking account of the secondaries produced by the incoming electrons through the mechanism of nuclear and close extranuclear encounters, for since we have shown that these are all low energy secondaries (else they would produce a sea-level latitude effect between Pasadena and Churchill), the energy of the incoming electron must be frittered away in quite a large number of relatively small steps, i.e., more or less uniformly, even by these nuclear encounters.

Nuclear photon absorption, on the other hand, whether brought about by photoelectric or by Compton encounters, consists in general—and we can also deduce this from our photographs—in the transfer of a large part of the energy of the photon to the ejected electron or electrons\*, thus yielding an exponential law of absorption.

The absorption, then, by the atmosphere, of incoming electrons of  $10^{10}$  e.V. and more, even though it might follow a law intermediate between that of linear and exponential absorption, must distinctly lean toward the former, and cannot possibly yield an altitude-ionization curve even remotely resembling that found experimentally from sea-level up to 4.5 m. in figure 1 and up to 0.6 m. in figure 4. *This constitutes the most general and the most cogent argument against the attempt to explain the non-field sensitive portion of the cosmic-ray ionization as due primarily to incoming high energy electrons, low energy electrons being barred out by the blocking effect of the earth's field.*

If, on the other hand, incoming photons are the main ionizing agents, then, whether the nuclear absorption is of the photoelectric type or the Compton type—and it is presumably the former—the mean energy of these photons must be of the same order of magnitude as the mean energy of the electrons produced by them, namely, say  $200 \pm 170$  million e.V. These figures are again consistent with the view that cosmic-ray photons have a penetrating power of the order of 100 times that of electrons of the same energy, for we have shown earlier that the effect of the main component of the cosmic-rays—that for which the absorption coefficient is of the order  $\mu = 0.5$ —just about reaches down to sea-level, while incoming electrons with such a range would require  $6 \times 10^9$  e.V.

(6) Again, evidence for the view that the ionization found in the atmosphere

\* Anderson, Millikan, Neddermeyer and Pickering, *Phys. Rev.* 45, 363 (7) (1933).

above sea-level cannot be produced wholly or even chiefly by  $10^{10}$  e.V. incoming electrons is found in the consideration that the penetrating power of such rays, both as to their primary and their secondary constituents, must obviously increase, or at most remain constant with increasing altitude, since the energy of the ionizing agents at the top of the atmosphere is  $10^{10}$  e.V. and at the bottom only  $4 \times 10^9$ . On the other hand, *the observed mean penetrating power actually decreases very markedly as shown in figure 5 between sea-level (10 m.) and 6 m. of water beneath the top.* It is difficult to see how this can be interpreted save in terms of photons of decreasing mean hardness with increasing altitude. Above 6 m., figure 5 shows that the penetrating power continues to decrease, but now much less rapidly, as though the ionization were now due mainly to a single photon band of coefficient of absorption somewhere near  $\mu = 0.5$ . This part of the curve of figure 5 must, however, be attributed to a mixture of causes, as shown in VII below. But with respect to similar data that we have taken in the equatorial belt, the foregoing argument may be stated thus. If the  $10^{10}$  e.V. and more—and no lower energies can get through the earth's magnetic field in Peru—were the only ionizing agents in the upper air, then the 10 cm. lead shield which we used there at 19,000 ft. (about half way to the top) could not have reduced the ionization in the chamber at all. Indeed, because of the secondaries formed within the lead it should have increased it. Instead it reduced the ionization to about one-third of its value without the shield—a fact apparently fatal to a particle theory.

#### §7. EFFECTS DUE TO THE FIELD-SENSITIVE PORTION OF THE INCOMING RAYS

All of the field-sensitive part of the ionization produced by cosmic rays is of course due directly or indirectly to incoming electrons. When we compute from the difference between the ordinates of the upper and lower curves of figure 1, the mean *apparent* absorption coefficient of the rays producing this ionization, it comes out roughly  $\mu = 1.0$  per m. of water. But we are not disposed to attach any physical significance to this *apparent* coefficient since it is due to the ionization produced at the ends of the ranges of electrons of widely varying energies. However, the rapid rise with altitude of the ionization between the upper and lower curves of figure 1 may be understood from the following considerations. We have already shown in §§ 4 and 5 why we regard the chief component of the non-field sensitive portion of the upper air ionization as due to a beam of incoming photons of energy of the order  $200 \pm 170$  million e.V. Such a beam would get into equilibrium with its secondaries at a depth below the top corresponding to the range of say 300 million e.V. which, since it takes  $6 \times 10^8$  e.V. to penetrate the atmosphere—10 m. of water—would be at a depth beneath the top of  $\frac{300}{6000} \times 10 = 0.5$  m. If the earth had no magnetic field and if the cosmic-rays were all of this frequency, there would at all latitudes be an exponential rise of the ionization with altitude at a rate somewhere near  $\mu = 0.5$  per m. of water right to the top if the beam were in equilibrium with its secondaries upon entering. On the other hand, if it entered as a *pure* photon beam, unmixed with any of its secondaries, the ionization would start from zero at the outer edge of the

atmosphere and rise to a maximum at 0.5 m. below the top and then fall off exponentially (with  $\mu = 0.5$ ) for increasing depths beneath the top.

The foregoing simple picture does not correspond to reality for at least two important reasons. First, the incoming cosmic-rays are distributed over a wide range of energies, the distribution curve at sea-level, according to Anderson\*, having a very weak intensity at energies as high as  $3$  or  $4 \times 10^9$  e.V., increasing rapidly with decreasing energy and going through a maximum at say  $8 \times 10^8$  e.V. This maximum, according to our own measurements herewith presented, moves rapidly toward lower energies with increasing altitude.

The second big factor of disturbance to the foregoing simple picture is the earth's magnetic field. If the photons of all the preceding energies were in equilibrium with their secondaries before entering the earth's magnetic field, this equilibrium would in any case be entirely destroyed by that field. At Panama, for example, all the electron secondaries below about  $8 \times 10^9$  e.V. are blocked out by that field, while at Spokane all electron secondaries down to say  $2 \times 10^9$  e.V. get through. This accounts for the rapid rise with altitude of the field-sensitive ionization represented by the difference between the Panama and the Spokane curves (figure 1). For, as Anderson's energy-distribution curves show, the number of incoming secondary electrons increases rapidly as the energy decreases from  $8 \times 10^9$  down to  $2 \times 10^9$  e.V. The result is not at all the linear rise with altitude discussed in § 6 (5) due to incoming electrons of a given energy above  $10^{10}$  e.V., but a very much more rapid rise due to the fact that e.g. those of  $2 \times 10^9$  e.V., first let in copiously through the field at magnetic latitude  $52^\circ$ , can only penetrate one-third of the way through the atmosphere and hence must do all their ionizing above that level. The effect here under consideration is very beautifully shown in figure 6, in which we present a comparison of the results of all the recent stratosphere flights. In the most northerly of these, the Fordney-Settle one—measurements by Millikan and Neher, the most accurate yet made because the balloon was essentially stationary for hours—the ionization near the top is seen to be very much larger than in the two Bowen-Millikan flights or indeed in the Regener flight, the first of which were made at about mag. lat.  $42^\circ$ , where no electrons of energy under about  $4 \times 10^9$  e.V. can get through the earth's magnetic field, while the Regener flight appears to have been made in about magnetic latitude  $48^\circ$ . There is still some experimental uncertainty with respect to these three lower curves of figure 6, but probably not enough to change the main conclusion here drawn.

We interpret also the *shapes* of the upper part of the curves made by Bowen and Millikan and by Regener at and near latitude  $42^\circ$  as due to the effect of the incoming electrons of between  $4 \times 10^9$  and  $8 \times 10^9$  e.V. For there are now no longer present the incoming  $2$  to  $4 \times 10^9$  e.V. secondaries to add to the ionization of the underlying photons in the upper part of the atmosphere, while those of  $4$  to  $8 \times 10^9$  e.V. are approaching the energies at which they penetrate the entire atmosphere and are therefore nearing the conditions that give rise to the linear ionization law discussed in § 6 (5). In a word, then, the altitude-ionization curve shown in figure 6 represents

\* Carl D. Anderson, *Phys. Rev.* **44**, 406 (1933).

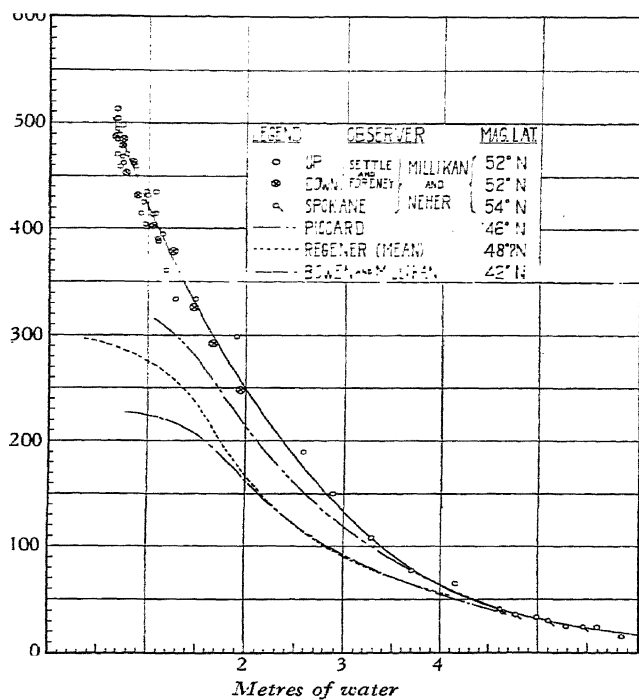


Figure 6.

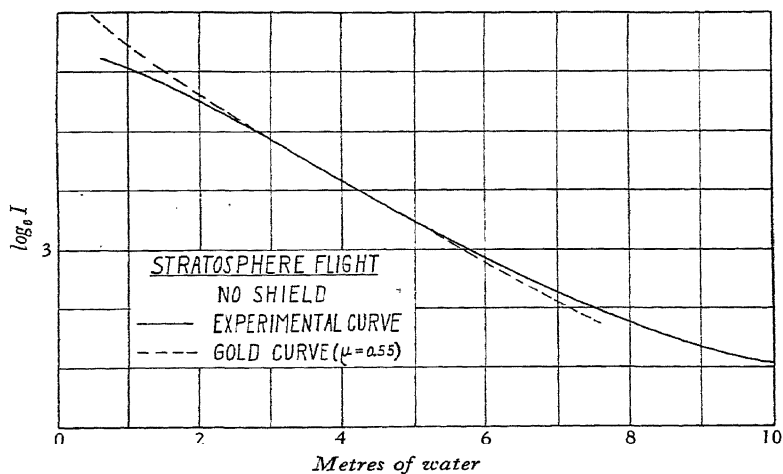


Figure 7.

a combination of the effects of the incoming photons of energies of the order  $200 \pm 170$  million e.V., and such incoming (extraterrestrial) secondary electrons as the earth's magnetic field will let through. These latter should be very strong ionizers in sufficiently northern latitudes and at great altitudes, but should be responsible for a relatively small part of the ionization in the equatorial belt. There they must be responsible for the longitude effect and the east-west effect, both found in the equatorial belt. We are hoping to do some higher altitude flights near the equator to test these conclusions further.

Figure 7 shows the results of the Fordney-Settle flight plotted on a log scale. This displays nicely (1) how from sea-level (10 m.) up to the height of Pike's Peak (6 m.) a sum of exponentials is needed to reproduce the observed ionization; (2) how a single absorption coefficient  $\mu = 0.55$  accounts for the ionization from 6 m. to 2.5 m. below the top, despite the complex character of the causes at work in this region, i.e., relatively low energy photons plus high energy ( $8 \times 10^9$  to  $2 \times 10^9$  e.V.) incoming secondary electrons; (3) how at a depth of about 2.5 m. below the top the constancy of the exponential rise with coefficient of  $\mu = 0.55$  breaks down, presumably because of the effect of the incoming (extraterrestrial) secondary electrons.

#### § 8. THE ORIGIN OF THE COSMIC RAYS

The conclusions of the preceding sections rest upon the two fundamental postulates, namely, (1) the general validity of the analysis of Epstein and Lemaître-Valarta as to the effect of the earth's magnetic field on incoming electrons; and (2) the validity of the evidence that in general the immediate ionizing agents in the production of cosmic-ray ionization are free positive and negative electrons, other ionizing agents not being necessarily absent entirely but at any rate exerting a negligible influence. The general *qualitative* validity of the first postulate will scarcely be questioned, and its quantitative validity is not of vital importance. For example, if the energies necessary to get through the earth's magnetic field were but half those computed by Epstein, the whole scale of electron energies would be reduced one-half without fundamentally modifying the reasoning or the conclusions.

The second postulate, that the immediate ionizing agents are electrons (+ and -) rests upon two sorts of evidence. First, we have studied most carefully thousands of cloud chamber photographs without finding any evidence for the presence in appreciable amount of protons or other heavy particles of any sort. If the Newtonian laws of encounter hold, protons, neutrons, or other heavy particles cannot transfer energies of millions and billions of e.V. to electrons such as we find in all our photographs. Only electrons and photons can possibly produce the types of effect shown in figures 7, 8, 9, 10, 11, 12, 13 and 14 of *Phys. Rev.* **45**, pp. 358-61. The combination of ionization, range and curvature shown in all these tracks fixes the ionizing agent in practically all cases as an electron (+ or -). Even more certain evidence on this point, however, is found in the fact that the multiplying factor due to raising the pressure in an electroscope is the same for  $\gamma$ -rays and cosmic-rays. We have tested this point directly or indirectly practically to the top of the atmosphere. This

means, as Millikan and Bowen first showed\*, that the fraction of ions formed that recombine is the same in both cases, and this can be true only if the immediate ionizing agent has in general the same ionizing power per cm. of path in the two cases.

Granting the correctness of these two postulates, it follows, for the reasons given in § VI, that the whole non-field sensitive portion of the ionization can scarcely be due to incoming electrons of an energy of  $10^{10}$  e.V. or more, and yet these are the only electron energies which the earth's magnetic field permits to penetrate into the equatorial belt. The very fact, then, that we need incoming photons at all to interpret cosmic-ray effects rather eliminates the possibility that the source of the cosmic rays is to be found in cosmic electrical fields which impart these  $10^{10}$  e.V. energies to electrons that fall through them.

So far, then, as we can now see, the only remaining possible source of these observed energies lies in atomic transformations taking place in accordance with Einstein's equation  $E = mc^2$ . The building of the common elements out of hydrogen is of course only a special case of this transformation of mass into radiant energy, and since such building of the helium atom releases 30 million e.V., of oxygen 116 million, of silicon 216 million, and of iron 460 million, there is no other origin which we can now see for the great absorption band found by us in the equatorial belt at about  $\mu = 0.5$  and modified by its mixture in the temperate belt with incoming secondary electrons into something like  $\mu = 0.55$ . This band alone seems to be responsible for about 90 per cent of the cosmic-ray ionization in the equatorial belt. Its energy is at least of the right order to fit this hypothesis, and no other source of energies of these magnitudes is yet in sight. It will be recalled that we made the condensation or clustering of hydrogen atoms into hydrogen "dust" in the intense cold of interstellar space a necessary antecedent to the act of building up. The conclusions of modern astronomers as to the existence of such interstellar dust are not out of line with this hypothesis.

But since the foregoing analysis requires a small number of cosmic-ray energies higher than  $10^{10}$  e.V., there seems to be no origin in sight for these save the sudden *complete* annihilation of whole atoms of helium ( $4 \times 10^9$  e.V.), carbon ( $12 \times 10^9$ ), oxygen ( $16 \times 10^9$ ), etc. We have already indicated in preceding papers how the extreme conditions of temperature and pressure existing in interstellar space might be favourable to the building up process, but we must now add the further suggestion that any condition which once starts the matter-annihilating process might in some cases stop at the part-way stage, or, in extreme cases, carry it completely through. If this possibility exists it would account for the observed uniformity of distribution of all the cosmic-ray bands, high energy as well as low, over the celestial dome, the most extraordinary characteristic of these rays. If we discard such suggestions of locating the events giving rise to cosmic rays in interstellar space we then seem to be forced to postulate, as Baade and Zwicky† do, some other sort of extra-

\* R. A. Millikan and I. S. Bowen, *Nature*, **128**, 583 (1931); R. A. Millikan, *Phys. Rev.* **39**, 397 (1932).

† W. Baade and F. Zwicky, *Proc. Nat. Acad. Sci.* **20**, 259 (1934).

ordinary conditions not depending on low temperatures and pressures, such as those existing in novae, to call forth both these partial and complete annihilation processes; or, again, we could take the alternative already suggested by other scientists and associate these annihilation processes with conditions existing at some preceding time when the universe was in a different state from that now existing. *At any rate, in the present state of our knowledge, both the partial annihilation of matter, like that exhibited in the building of the common elements out of hydrogen, and the complete annihilation of atoms, seem to be called for to account for the energies actually found in the cosmic rays.*

All of the foregoing work has been made possible through a grant from the Carnegie Corporation of New York, administered by the Carnegie Institution of Washington. We desire to express our deep appreciation for this assistance.

## A STUDY OF COSMIC-RAY BURSTS AT DIFFERENT ALTITUDES

By ARTHUR H. COMPTON AND RALPH D. BENNETT

Chicago and Massachusetts Institute of Technology

*ABSTRACT.* Experimental work on cosmic-ray "bursts" is described. In particular it is shown that they are not due to ionization by collision in the apparatus. Some bursts as large as  $2 \times 10^8$  ions have been observed with low voltage, and as great as  $7 \times 10^9$  at high altitudes with saturation voltage.

BURSTS of ionization caused by cosmic rays have been studied in a 20 litre steel chamber filled with argon gas at 50 atmospheres. The chamber was protected by a layer of lead shot equivalent to 12 cm. of solid lead. The average cosmic-ray ionization was balanced by the ionization in an auxiliary chamber produced by the  $\beta$ -rays from metallic uranium. In this way the bursts were shown by departures from the steady position of the electrometer needle.

Bursts were observed when the potential across the ionization chamber was as low as 18 V. Under these conditions there is no chance for ionization by collision to play a part in the phenomenon, thus demonstrating the reality of the bursts. Though with this low voltage some re-combination occurs, resulting in a smaller number of ions being collected by the electrodes, nevertheless single bursts of as large as  $2 \times 10^8$  ions have thus been observed.

With voltages sufficient to produce saturation, the number of ions collected per burst has been as great as  $10^9$  at sea-level or  $7 \times 10^9$  at high altitudes. This latter figure represents an energy equal to that of the total mass of an atom of atomic weight 20. It thus seems unlikely that the bursts are to be ascribed to any kind of nuclear reaction.

The frequency of the bursts is found to increase more rapidly with the altitude than does the intensity of the total cosmic-ray beam. This result is in accord with the preliminary findings which we have previously reported.



# THE CONNEXION BETWEEN COSMIC RADIATION AND ATOMIC DISINTEGRATION

By G. HOFFMANN

Halle/Saale

**ABSTRACT.** The paper deals with the bursts of ionization ("Stösse"), which were first observed by the author in 1927. These have been shown to be increased when the apparatus is surrounded by a lead shield, but from the frequency distribution it appears that they are not merely unusually large "showers." Arguments are given to show that they are in no way due to instrumental defects, nor to ionization by collision.

Observations show that the position of the maximum in the frequency curve is characteristic of the material of the shield, and that if a double shield is used, both maxima can be distinguished. The bursts are not due directly to the hard group of cosmic rays.

The stoss-mechanism is not yet definitely explained, though neutrons and positive and negative electrons probably play a part in the phenomena.

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COSMIC radiation is geophysically and astronomically a very interesting phenomenon, which has also special importance for nuclear physics because here quanta of energy appear, which for us so far are unattainable in laboratories. Between the million e.V. quanta of rays which are produced by high tension or by radioactive processes, and the milliard e.V. or even higher quanta of cosmic radiation, a great gap remains. The size of this gap makes the interpretation of the phenomenon observed in connexion with cosmic radiation very difficult and gives us many riddles to solve.

Where large quanta come into action, smaller quanta of every size will result by division, and it is at once seen that the process of atomic disintegration will result from it; it is only a question whether it will be in an observable degree. Some researches made in Halle a short time ago seemed to lead to positive results\*. We are continuing these measurements and are making observations alternately in the mine and the laboratory. I had hoped to be able to bring further particulars and results of these experiments, but we have not progressed far enough on account of the very obvious technical difficulties.

Therefore I should like to discuss another phenomenon, which I think involves a distinct relation between cosmic radiation and atomic disintegration. I refer to the bursts of ionization, which have become known by the German designation of "Stösse."

The first results ever recognized as the new striking phenomenon known as "Stoss" is shown by the record taken in the year 1927 (figure 1). This sheet was taken by the apparatus which later on was used in the Upper Engadin for per-

\* G. Dieck, *Z. f. Phys.* 90, 71 (1934).

manently registering the cosmic rays: a pressure bomb containing 50 litres of  $\text{CO}_2$  under a pressure of 30 atmospheres, and with 10 cm. of lead shielding. The uniform action is compensated by influence-current to 1-2 per cent. The length of the kick is equivalent to about  $4 \times 10^6$  ions. Naturally I searched long for an instrumental defect.

The second record of a stoss occurred at a height of 2450 m., and I showed it as such at the Physical Congress in Zürich in 1929 (figure 2, between 2 and 3 a.m.).

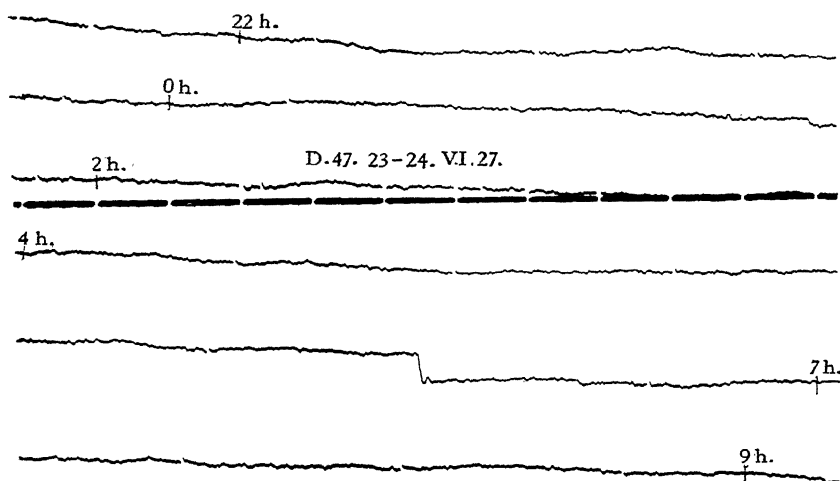


Figure 1. Record of first observed stoss (1927).

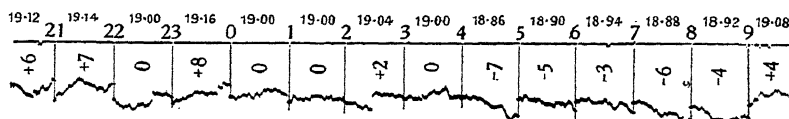


Figure 2. Stoss observed in October 1927 on Muottas Muraigl.

We then convinced ourselves that these stösse were never registered by the same apparatus in a deep mine, and by this proved clearly that this effect pertains to cosmic rays. The stösse are rare, our large apparatus marking only a few in the course of 24 hours.

In the year 1932 Dr E. G. Steinke\*, with whom I have long worked, discovered that the number of stösse per day was connected with the shielding, the ratio with and without the lead shielding of 10 cm. thickness being about 1.7 : 1. These results were shortly afterwards confirmed by W. Messerschmidt† with our apparatus at Halle.

\* E. Steinke and H. Schindler, *Z. f. Phys.* **75**, 115 (1932).

† W. Messerschmidt, *Z. f. Phys.* **78**, 668 (1932).

Then in 1933 Blackett and Occhialini\* found with their beautiful automatic Wilson chamber that in the cosmic rays multiple tracks, called showers, often appear, and very instructive Wilson photographs showing multiple tracks of electrons and positrons were obtained by Anderson, Locher and Kunze†. It was natural to connect the great quantity of ions in the bursts with the multiple tracks, but it has been proved that this cannot be done quite so directly. Even though it is

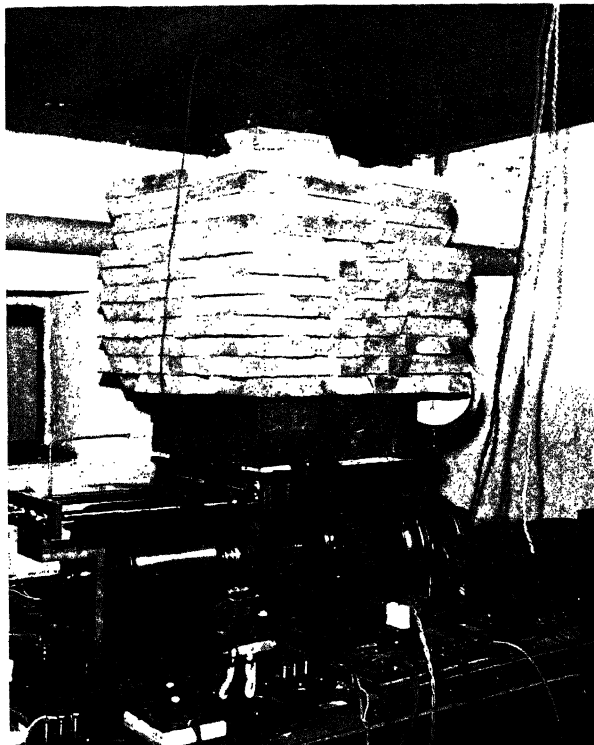


Figure 3. Messerschmidt's apparatus.

difficult to take exact statistics, we can show by the results of many Wilson photographs—since from the probability of the number of the simple- double- treble- etc. tracks found, we can infer the frequency of the great stösse, whence from the number of ions we can calculate, that several hundred tracks would have to be present at the same time,—that this occurs so much too seldom that the probability of observation is practically nil. Millikan, Anderson and Neher‡ have from this recently drawn the conclusion that there are three kinds of cosmic ray

\* P. M. S. Blackett and G. P. S. Occhialini, *Proc. R.S.* **139**, 699 (1933).

† C. D. Anderson, *Phys. Rev.* **41**, 405 (1932); *Phys. Rev.* **44**, 406 (1934); G. L. Locher, *Phys. Rev.* **39**, 883 (1932); P. Kunze, *Z. f. Phys.* **83**, 1 (1933).

‡ R. A. Millikan, C. D. Anderson and H. V. Neher, *Phys. Rev.* **45**, 141 (1934).

fluctuations—(1) bursts, (2) showers, (3) free-electron shots—and have then set aside the bursts as instrumental accidents. But as they themselves have observed, that these instrumental accidents occur more frequently with shielding and are also more numerous in the high mountains, they must be indirectly caused by cosmic radiation, and the authors explain them as due to the occasional occurrence of ionization by collision, which increases the showers into bursts. I think that this explanation must be absolutely rejected. The strength of the electric field in our apparatus is far removed from the values for ionization by collision. Further it is easy by suitable tests to demonstrate that the stösse must have another foundation. Bennett\* has thoroughly examined these possibilities. The result is that “in apparatus with normal receivers (as in Compton-Bennett and other types of cosmic ray ionization chambers) no reasonable assumption of space-charge density leads to field

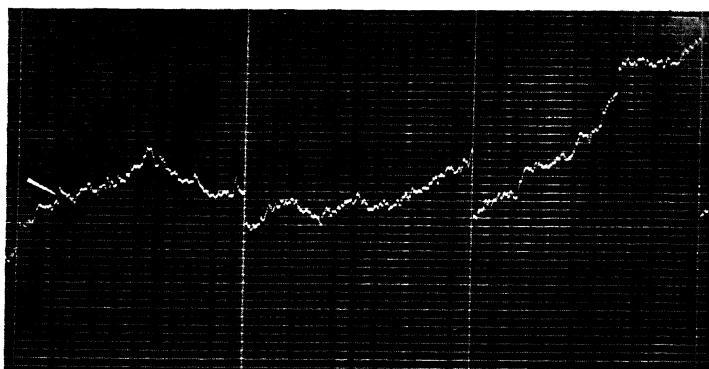


Figure 4. Records from Messerschmidt's apparatus. The record covers three hours; 10 minutes after the beginning there is a stoss of 1.5 divisions (marked by the dart); none in the second hour; in the third hour, there is a stoss of 2.5 divisions after 38 minutes.

strengths required for ionization by collision; that in apparatus of the Millikan-Neher type a remote possibility exists that sharp points may produce gradients dangerously near the breakdown point. Such instruments can and should be tested in this respect before being used for statistical work.”

According to a private communication from W. G. F. Swann in the Franklin Institute, these large bursts were obtained even “with potential differences as low as 4.5 V., which even with the aid and conspiracy of all known phenomena, could not give rise to bursts of ions by ionization by collision.”

According to another private communication from Prof. A. H. Compton, “the new recording meter for cosmic rays with only 18 V.—less than the ionizing potential—gives bursts.”

But the reality of the bursts as independent phenomena is best proved by new properties which follow regular laws. In this connexion there are the new results of the work of my collaborator W. Messerschmidt. We use pressure ionization

\* R. D. Bennett, *Phys. Rev.* 45, 491 (1934).

chambers of a moderate size and observe the ionization current with the highest possible electrometers sensitiveness, using a compensation arrangement. The ionization chamber must be of a *medium* size; large enough to contain a sufficient number of ions from one burst, and on the other hand not too big, in order that the increasing statistical fluctuations caused by the irregular succession of the ionizations through various corpuscular tracks may not conceal the effect of the bursts. As an instrument for observation, a string-electrometer was used. 1 mm. of the record equals  $0.5 \times 10^6$  ionic charges. The path of the corpuscles within the chamber (converted to normal pressure) is 15 metres. With the paper-speed used, the momentarily produced quantities of ions show up clearly against the waviness of the statistical fluctuations. This is most rapidly seen on looking at a record (figure 4).

With this apparatus we can produce very reliable statistics on the sizes of the stösse, especially in regard to the smaller stösse and their demarcation compared to the fluctuations.

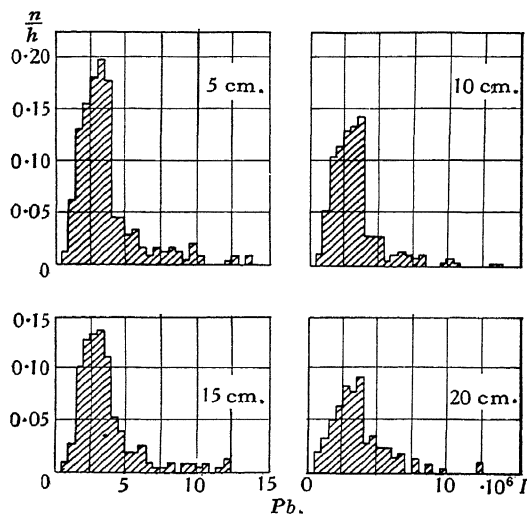


Figure 5. Stösse from lead.

Figure 5 shows four lead-registrations. In each diagram there are the results of about 250 hours of recording. On the whole 800 stösse have been recorded. With increasing thickness of the shielding the number of stösse becomes less. The position of the maximum remains at  $I = 3.8 \times 10^6$ .

Figure 6 shows aluminium-stösse. The number of the stösse increases up to 30 cm. thickness of the shielding and has then about doubled itself. The maximum is essentially lower than with lead, about  $2 \times 10^6 I$ .

Figure 7 shows the result of the combination of two different shieldings. Here there was 9 cm. aluminium inside, and 10 cm. lead outside. Beside the aluminium maximum, the lead maximum is indicated.

In addition to these measurements, observations with iron and carbon have been executed. The results with iron lie between those of aluminium and lead. With carbon, for which briquets of coal were used, the stösse were essentially smaller than with aluminium, and they become more difficult to distinguish from the statistical fluctuations.

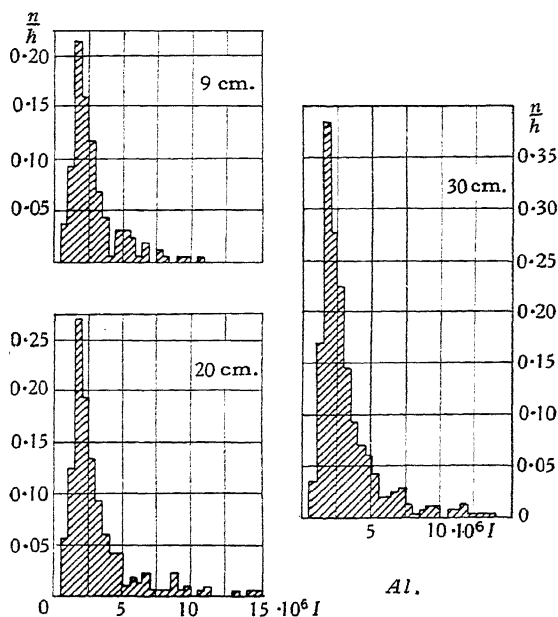


Figure 6. Stösse from aluminium.

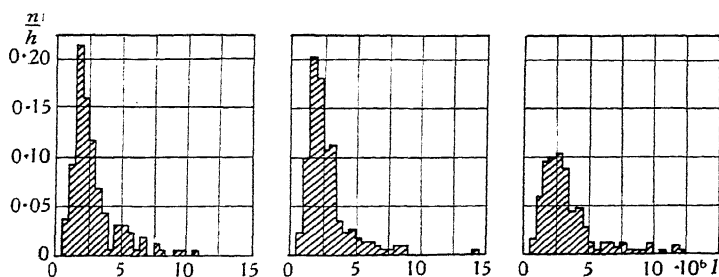


Figure 7. Stösse from aluminium and lead.

The observations show firstly, that we are dealing with well-defined phenomena. The various shielding materials give characteristic positions of the maxima. Also something can be stated about the frequency of the stösse. As the number of the stösse decreases with increasing thickness of the lead shielding, we must not make the hardest components of the cosmic rays responsible for the origin of the stösse,

but a medium radiation, the hardness of which lies indeed considerably beyond the hardness of the radiation of the radioactive phenomena. If we estimate this hardness by Messerschmidt's results, it is about equal to the hardness of the radiation which has the greatest intensity at the earth's surface.

The stoss-mechanism remains unexplained. At present I should take the view of Swann and Locher\*, that the primary stoss action liberates neutrons; the number or the efficiency of these neutrons increases with the ordinal number of the shielding material. However, we can also conclude from the results that positrons and electrons are formed during this process. The two interpretations are not mutually exclusive from the standpoint of present-day knowledge. The documents about the nature of the stösse are not finished, but they do exist.

\* G. L. Locher, *Phys. Rev.* **44**, 779 (1934).

## SOME RESULTS ARISING FROM THE STUDY OF COSMIC RAYS

By B. ROSSI

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*ABSTRACT.* Reference is made to experiments in which the numbers of coincidences between the discharges of two Geiger counters placed vertically one above the other are observed. If a lead screen is placed between the two, the absorption of the cosmic rays can be measured. It is found that a 30 per cent decrease occurs in the first 12 cm. of lead, but that the diminution thereafter is extremely slow, thus indicating that there are two groups, a hard group and a soft one. The legitimacy of this method has recently been disputed, and various experiments with three counters arranged in different ways are described; they prove without doubt that the previous results are substantially correct.

At sea-level, the hard group is about twice as intense as the soft, whereas at 2370 m. altitude (and a magnetic latitude of  $11^{\circ} 30'$ ) they are about equally intense.

The hypothesis that the particles of the hard group are present in the cosmic rays before they reach the earth is examined in detail, and it is considered that the observed azimuthal and latitude effects support it strongly. They are interpreted in the light of Störmer's theory of the motion of a charged particle in the earth's magnetic field; from this theory, combined with the observations, it is deduced that an appreciable fraction of the particles reach the atmosphere with an energy between 10 and  $23 \times 10^9$  e.V. It is also deduced that the minimum energy loss of cosmic particles is about  $3 \times 10^6$  e.V. per gm./cm<sup>2</sup>.

The particles of the soft group are considered to be of secondary origin, since they are found at sea-level; and any such particles which entered the atmosphere would be absorbed before reaching sea-level.

It is shown that the particles of the hard group cannot be responsible for the "showers" which are produced in matter by cosmic radiation; in fact, the shower-producing radiation has quite different absorption properties from the primary radiation. No definite conclusion is yet reached as to this shower-producing radiation.

In an appendix added in October 1934, the author describes more accurate experiments on the intensities of the primary and secondary corpuscular radiation and of the frequency of shower production. The conclusion is drawn from these, and from previously known results, that the hard group of the cosmic radiation is incompetent to account for the whole of the observed effects. There must in addition be at least one other (softer) component, which is identified with the shower-producing radiation. The possibility that yet other components of the radiation are present is not, however, ruled out.

THE numerous experimental results which have lately been obtained in connexion with cosmic rays at different stations and by different methods have brought out some properties of so singular and so unexpected a nature that the general problem of the origin of the cosmic rays and of the sequence of processes by which they exhaust their enormous energy in matter now seems farther from a solution than it did at the beginning of these researches.



Amidst the crowd of experimental data and of often contradictory interpretations, we may nevertheless pick out a certain number of special results which can be considered as definitely established, and which it may be worth while to enunciate explicitly, in order to see clearly on what foundations we can build with some probability that we shall not see the edifice collapse. This is what I shall attempt to do, limiting myself, however, to a field where I have some personal experience.

### §1. COSMIC PARTICLES

First of all, we can state that the immediate result of observation is an ionization produced by electrified particles, which can be enumerated by help of a Geiger or Geiger-Müller counter, and whose paths can be photographed in a Wilson chamber.

There is full agreement on this point; but it must be said that we are not here dealing with a characteristic property of cosmic rays. This is, as a matter of fact, what happens with any rays if their individual energies are considerably greater than the ionization energy of the gas. Even  $\gamma$ -rays and neutrons, for example, ionize through the intermediary of electrons and recoil nuclei. The difference consists solely in the energy, which, for cosmic radiation particles, is much greater than for particles from any other known radiation. Thus the metallic walls of the counters, which stop practically all the secondary electrons of  $\gamma$ -rays, are almost perfectly transparent to cosmic particles. In consequence, by arranging several counters in a straight line, they can all be traversed by the same cosmic particle; this event is marked by simultaneous discharges in the counters (a coincidence).

If a screen is placed between the counters, then the cosmic particle, in order to traverse the counters, is evidently forced to pass through the screen also. As Bothe and Kolhörster first showed<sup>(1)</sup>, the absorption of the cosmic particles can thus be measured by observing the diminution of the coincidences due to the interposition of a screen between the counters. This measurement could not be made by simply observing the falling off of the discharges in a single counter above which the absorbing screen was placed; for in this case, those particles which had been produced in the screen itself by a non-ionizing radiation would be recorded, as well as the particles capable of traversing the screen. The former, on the other hand, are not detected by the method of coincidences, since they cannot pass through all the counters, because the screen in which they are formed is placed between the counters themselves.

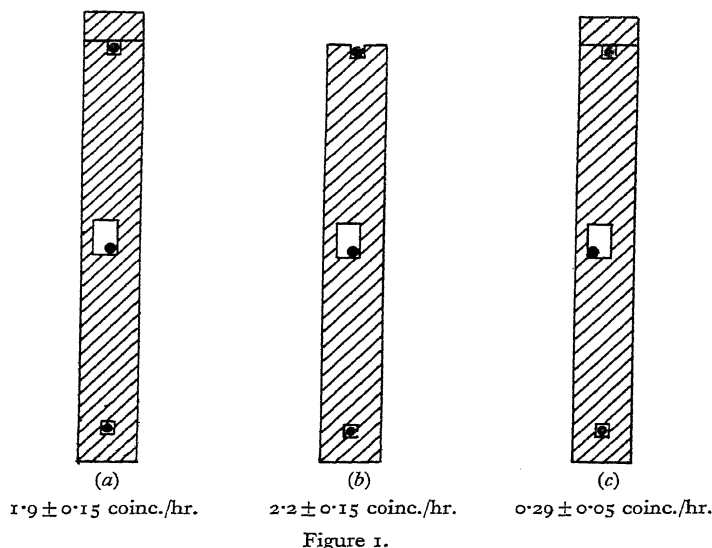
It is found that on increasing the thickness of the screen, the frequency of the coincidences at first falls off fairly rapidly, being reduced within about 10 cm. of lead to some 70 per cent of the initial value (at sea-level). But afterwards the diminution becomes extremely slow: with 1 m. of lead, more than 50 per cent of the coincidences that are observed with 10 cm. are still found<sup>(2)</sup>.

All these facts are well established, and it would not be worth while recalling them, if doubts had not recently been expressed as to the legitimacy of the method of coincidences<sup>(3)</sup>.

What is disputed is whether the observed coincidences, with several centi-

metres of lead between the counters, are really due to the passage of the same particle through all the counters.

I could certainly not have rejected this objection as being *a priori* unjustified, since I had myself shown that numerous coincidences can occur among three counters not in a straight line, owing to the simultaneous arrival of two or more secondary particles<sup>(4)</sup>; besides, the beautiful experiments of Blackett and Occhialini<sup>(5)</sup> have just shown us that the secondary particles are produced in "showers," each containing many particles and having in consequence a great probability of discharging a counter near which they are formed. I must, however, confess that I should have been very surprised if, in the actual conditions of the absorption measurements, any large fraction of the observed coincidences had been produced by showers. In



any case, the following experiment, which has recently been carried out in my laboratory<sup>(6)</sup>, settles the question, in my opinion.

Three Geiger-Müller counters (figure 1 (a)), 2.5 cm. in diameter and 25 cm. long, are arranged one above the other with their axes in the same vertical plane. Seven cm. of lead are placed above the first counter; 45 cm. of lead between the first and second; 45 cm. of lead between the second and third. In these conditions, about 1.9 coincidences per hour are observed. These coincidences could be due either to ionizing particles passing through the three counters, and consequently through the interposed 90 cm. of lead, or else to non-ionizing rays which produce three different showers of secondary particles above the three counters, each shower exciting one counter.

It is easy to decide experimentally between these two possibilities.

(1) If we suppress the lead screen above the first counter (figure 1 (b)), then on the first hypothesis we should expect a slight increase in the number of coincidences; on

the second hypothesis, a considerable reduction is to be expected, since the probability of a shower being produced sufficiently near the counter (i.e. in the air or in the wall of the counter itself) becomes exceedingly small. In accordance with the first hypothesis, about 2.2 coincidences per hour are found under the conditions of figure 1 (*b*).

(2) If we displace the middle counter 3 cm. laterally, the screen above the first counter being back in its place (figure 1 (*c*)), then on the first hypothesis we must expect the number of coincidences to be reduced almost to zero; on the second hypothesis, on the other hand, the number of coincidences should hardly alter. In agreement with the first hypothesis, about 0.29 coincidences per hour are found under the conditions of figure 1 (*c*). These coincidences (which, moreover, cannot be considered as fortuitous, since with one of the counters moved to some distance, only one coincidence was observed in 96 hours) could be produced by showers; but they could also be explained by a slight diffusion of the ionizing corpuscles in the lead. In any case, we can be certain that the greater part of the observed coincidences in conditions (*a*) and (*b*) are really due to ionizing particles passing through 90 cm. of lead.

It follows that the application of the method of coincidences to the measurement of the absorption of cosmic particles in matter is legitimate, and that the results obtained by this method are, at least in outline, correct. These results can be summarized as follows: The cosmic particles observed at sea-level or on mountains are divided into two sharply separated groups; a "soft" group, for which the mean penetrating power is equivalent to some centimetres of lead, and a "hard" group, for which the mean penetrating power is some metres of lead.

As we have just seen, at sea-level the hard group is about twice as intense as the soft group; at a height of 2370 m., on the other hand (at a magnetic latitude of  $11^{\circ} 30'$ ) the hard and soft groups seem to have about the same intensity, according to our experiments at Eritrea.

As regards the absorbing power of different substances for cosmic particles, it seems to be approximately proportional to the density; no influence of atomic number has, up to the present, been found.

## §2. ORIGIN OF THE HARD GROUP

Some of us have long been convinced that the particles belonging to the group of longest range were not produced in the atmosphere by a non-ionizing primary radiation, but were to be considered as belonging to the primary radiation itself<sup>(1,2)</sup>.

It had never been possible, as a matter of fact, to show the formation of these particles in matter, whilst that of the softer corpuscles had been observed.

This point of view has been fully confirmed by recent experiments which show in a direct manner the influence of the earth's magnetic field on the cosmic radiation.

It is not easy to calculate this effect exactly by theory; but, as I showed four years ago<sup>(8)</sup>, its general nature can be deduced in a very simple way from the

equations given by Störmer for the motion of an electrified particle in the field of a magnetic dipole. One finds precisely that electrified particles approaching the earth from a distance large compared with its radius are so deflected by the earth's magnetic field that only those with most energy can reach the surface of the earth, at any arbitrary point and from any given direction. Those of least energy, on the other hand, can only arrive out of the equatorial belt bounded by the parallels corresponding to a northern or southern magnetic latitude, which increases with decreasing energy of the particles. For a radiation with a continuous energy spectrum, we must therefore anticipate a gradual reduction of intensity from the pole towards the equator (latitude effect).

As we approach the parallel where particles of a given energy cease to arrive, the number of particles does not diminish equally in all directions; a "shadow cone" is formed (i.e. an angular region within which the particles are no longer observed) which opens out gradually until it fills the whole sky. The shadow cone is open towards the east or towards the west according as the particles are positively or negatively charged. For a radiation of charged particles with different velocities, we must therefore expect a dissymmetry with respect to the plane of the magnetic meridian; the particles being more numerous on the west side if their charge is positive, and on the east side if they are negatively charged (azimuthal effect).

Actually, the measurements of J. Clay originally<sup>(9)</sup>, and later those of A. H. Compton<sup>(10)</sup>, H. Hörlin<sup>(11)</sup>, P. Auger and L. Leprince-Ringuet<sup>(12)</sup>, I. Ranzi, S. de Benedetti and myself<sup>(13)</sup> and of yet other physicists, have shown with complete certainty that the intensity of the cosmic radiation diminishes on approaching the magnetic equator.

As to the azimuthal effect, which I had sought for in vain<sup>(14)</sup> at Florence in 1931, it was demonstrated last summer in lower magnetic latitudes by the almost simultaneous experiments of T. H. Johnson<sup>(15)</sup>, L. Alvarez and A. H. Compton<sup>(16)</sup>, myself<sup>(17)</sup>, P. Auger and L. Leprince-Ringuet<sup>(12)</sup>, J. Clay<sup>(18)</sup>, etc.; it turned out that for a given zenith distance the intensity is appreciably greater on the west than on the east. We must conclude therefore that a part of the primary cosmic radiation really consists of charged particles, and that these particles (at any rate most of them) are positively charged.

That it is indeed the hard group of cosmic particles and not the soft one which is deflected by the earth's magnetic field is proved in the most direct manner by noting that the azimuthal dissymmetry becomes greater if the particles of least energy are filtered out. As is well known, the measurement of the azimuthal effect is carried out by means of two or more Geiger-Müller counters with their axes parallel and horizontal and their centres in a straight line, which is directed alternately towards the west and the east, without altering its inclination to the vertical. Now at Eritrea (magnetic latitude  $11^{\circ} 30'$ , height 2730 m.), de Benedetti and I<sup>(7)</sup> found a ratio of  $1.32 \pm 0.03$  between the frequencies of the coincidences in the two directions, with a zenith distance of  $45^{\circ}$  and with 8 cm. of lead between the counters; without a screen this ratio is only  $1.19 \pm 0.02$ .

It results from the theory that in a magnetic latitude of  $11^{\circ} 30'$ , no positive

particle of energy less than  $22 \times 10^9$  e.V. can reach the surface of the earth in a direction at  $45^\circ$  to the vertical and oriented towards the east; whereas towards the west, and at the same zenith distance, the minimum energy of positive particles is  $10.5 \times 10^9$  e.V. The observed azimuthal effect thus shows that a considerable fraction of the cosmic particles reach the atmosphere with an energy between  $10.5 \times 10^9$  and  $22 \times 10^9$  e.V.\* These extremely high values of the energy which are deduced from the "magnetic analysis" of the cosmic particles made by means of the earth's magnetic field are quite in agreement with the great penetrating power of the particles found by the method of coincidences.

Another interesting consideration arises in connection with the influence of the earth's magnetic field. The experiments on the latitude effect show that the diminution in the intensity of the cosmic radiation commences, at sea-level, at a magnetic latitude of about  $50^\circ$  where, according to the theory, particles of less than  $3 \times 10^9$  e.V. are prevented from reaching the surface of the earth. From this it follows that  $3 \times 10^9$  e.V. represents the minimum energy possessed on entering the atmosphere by the primary cosmic particles observed at sea-level. It is quite natural to think that it is the atmospheric absorption itself which cuts off the energy spectrum of these particles at  $3 \times 10^9$  e.V. Since the atmosphere has a thickness of about 1000 gm./cm<sup>2</sup>, we may conclude that the energy loss of cosmic particles in matter is about  $3 \times 10^6$  e.V. per gm./cm<sup>2</sup>. Now Blackett and Occhialini<sup>(5)</sup> and Anderson<sup>(19)</sup> have measured directly by means of a Wilson chamber with a metal screen, the decrease of energy of cosmic particles passing through matter, and have found a value very close to that which we have just suggested; this agreement confirms our deductions.

We may remark in passing that probably the absorption of the cosmic particles in matter does not take place solely by a gradual slowing up due to continuous ionization along the path; there are grounds for supposing that from time to time closer collisions occur (probably nuclear collisions), in which the particle loses an appreciable fraction of its energy. The range in matter of several particles all having the same initial energy would thus in general be different.  $3 \times 10^6$  e.V. represents the energy dissipated per gm. per cm<sup>2</sup> in the process of ionization; consequently by dividing the energy of the cosmic particles by  $3 \times 10^6$ , we obtain, not the *mean* range, but the *maximum* range of the particles; that is, the range of those particles which, by chance, experience no nuclear collision.

### §3. ORIGIN OF THE SOFT GROUP

The particles belonging to the "soft" group are certainly, unlike those belonging to the hard group, of a secondary origin. This can be established, among other ways, as follows. At a height of 2370 m. (according to our experiments at Eritrea<sup>(7)</sup>), the soft group of cosmic particles is entirely absorbed by 8 cm. of lead (i.e. the absorption curve for the corpuscular radiation, obtained by the method of coincidences, falls extremely slowly after 8 cm. of lead; see figure 2). None of the particles

\* These figures are calculated for particles whose rest-mass is negligible as compared with the relativistic mass, which is the case for positrons and, approximately, for protons.

of the soft group observed at 2370 m. can then reach sea-level, seeing that the intervening layer of air is equivalent by weight to 22 cm. of lead, and seeing also that the absorption of the cosmic particles is, at least approximately, proportional to the superficial mass of the screen. The rather numerous group of soft particles observed at sea-level must then have been formed in the layer of air lying between sea-level and a height of 2370 m. (It is evident, in other words, that if new soft particles were not produced in the atmosphere, the absorption of the corpuscular radiation produced at sea-level by 4 cm. of lead, for example, would equal the absorption observed at 2370 m. between 22 and 26 cm. of lead. Actually, the former is about ten times the second, the absorption curve in the first few centimetres of lead at sea-level having the form shown dotted in figure 2.)

Again, we now have direct proof that cosmic radiation produces a secondary corpuscular radiation in matter. The first experiment which showed definitely the

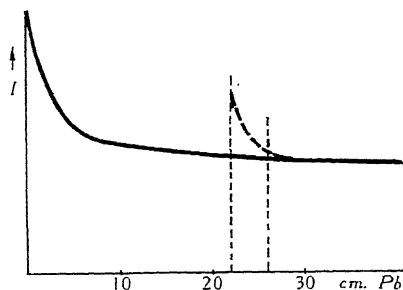


Figure 2.

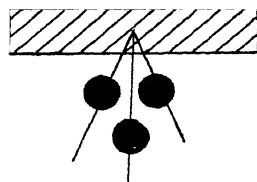


Figure 3.

existence of this secondary radiation was made by the aid of three Geiger-Müller counters so arranged that a single particle could not pass through them all (figure 3)<sup>(4)</sup>. Every coincidence between the counters must then denote the simultaneous arrival of two or more particles. Actually, with this arrangement, appreciably more coincidences were observed than could be explained by mere chance; and, what is more significant, this number increased several fold on bringing a lead screen near.

In matter there is therefore a production of secondary particles; the few coincidences observed without the screen can reasonably be explained by the secondary particles produced in the walls of the counters themselves, and in the supports, etc.

The extremely interesting results on the production of secondary radiations obtained by Blackett and Occhialini<sup>(5)</sup>, and quite recently by Anderson, Millikan, Neddermeyer and Pickering<sup>(20)</sup> by means of a Wilson chamber which is automatically operated by the passage of cosmic particles, are well known. These results have taught us, as I recalled just now, that the phenomenon is much more complex than could have been expected originally. The secondary particles originate in groups ("showers"), following, probably, on encounters with atomic nuclei. A shower, however, is not formed, it appears, in a single process, but in several successive processes, for the associated secondary particles do not all radiate from a

common centre. Among these particles, negative and positive electrons are found in approximately equal numbers; which suggests that the phenomenon of materialization of energy plays an important part in the production of the showers<sup>(21)</sup>.

I do not enter into the details of these experiments, since Messrs Blackett and Millikan will instruct us much more competently in this matter. Again, for a similar reason, I shall not discuss "transition phenomena" which were discovered and have been carefully studied by Hoffman and his pupils, and of which the explanation also involves a secondary radiation<sup>(22, 23, 24, 21)</sup>. I would rather set out some results which have been obtained by the method of coincidences, and which have a certain interest, particularly in relation to the problem of the origin of the showers.

The hypothesis which most naturally suggested itself was the obvious one of identifying the radiation which produced the showers with the hard group of cosmic particles, whose primary origin we have already accepted. But it was soon seen that this hypothesis did not suffice to explain the observed facts. Consider for example

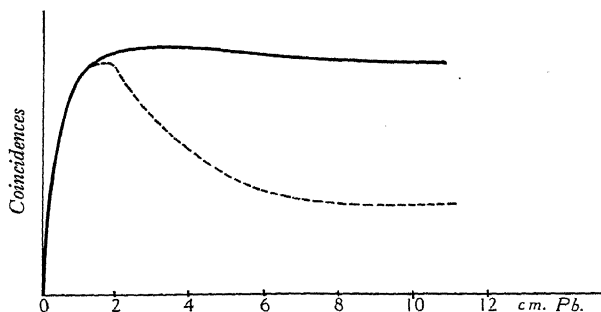


Figure 4.

the following experiment. Three counters are placed as shown in figure 3, with a lead screen above them, which is gradually increased in thickness; for the various screen thicknesses, the frequency of triple coincidences is measured; the variation of this frequency gives information on the way that the number of showers emerging from the plate varies with its thickness.

If the showers were formed by the hard corpuscular radiation and if the shower particles could be identified with the soft corpuscular radiation, then the curve connecting the frequency of the coincidences with the thickness of the screen would have the general form shown by the continuous line in figure 4. That is, the coincidences would increase rapidly at first, then reach a maximum frequency at a thickness of a few centimetres (corresponding to the range of the secondary particles) and then diminish very slowly, following the law of absorption of the primary corpuscular radiation.

Experiment, on the contrary, gives the dotted curve, whose most striking characteristic is the rapid fall which follows the maximum<sup>(25)</sup>; this indicates in an unequivocal manner that the radiation producing the showers is absorbed much more rapidly by lead, than the primary cosmic particles. (We may note in

passing that, the penetrating power of this radiation being of the same order of magnitude as that of the particles which it produces, the position of the maximum of the curve depends on these two penetrating powers, and not only on the penetrating power of the secondary radiation, as in the case of a very penetrating primary radiation.)

The most significant results, perhaps, have been those obtained by studying the different ways in which the phenomenon occurs in substances of different atomic numbers. Firstly, by placing above the counters screens formed from different elements and all having the same mass per unit area (which must be rather small, so that there shall be no appreciable absorption either of the radiation producing the showers or of the particles of the showers themselves), we may examine how the number of showers produced in a unit thickness ( $\text{gm. per cm}^2$ ) of matter varies with the atomic number. All the measurements (on Pb, Fe, Al in my original experiments<sup>(25)</sup>, and in those of Fünfer<sup>(26)</sup>; on Pb, Sn, Al in the experiments of Sawyer<sup>(27)</sup> and on Pb, Sn, Zn, Cu, Fe, S, Al, C in the work of Alocco and Drigo<sup>(28)</sup>), agree in showing a rapid increase of the showers with rising atomic number.

The absorption of the shower-producing radiation can also be measured by placing above the counters a lead screen of thickness slightly greater than the abscissa at the maximum of the curve in figure 4, and then measuring the diminution in the number of coincidences obtained by adding above this screen, others all with the same mass but with different atomic numbers. It is found that the absorption of the radiation producing the showers increases with the atomic number, i.e. it increases when the number of showers produced increases<sup>(21, 24)</sup>. More precisely, as Gilbert pointed out<sup>(32)</sup>, the cross-section of the different atoms for the shower-producing radiation seems to be proportional to the square of their atomic number.

The shower-producing radiation has then altogether different properties from the corpuscular radiation (for which the absorption in different substances is approximately proportional to the mass), which leads us (as I pointed out last year in Zürich<sup>(21)</sup>) to consider the cause of the showers as a new radiation, or, more precisely, as a new component of the cosmic radiation which must be added to the hard and soft groups of particles, of which we were speaking just now. The production of showers seems to be the normal mode of interaction of this radiation with matter, and consequently is the primary cause of its absorption.

The connexion between the shower-producing radiation and the soft group of cosmic particles is clear: the latter are, in fact (at least as regards the majority), particles from showers, i.e. secondary rays from the shower-producing radiation.

As to the hard group, it is certainly not composed of particles from showers (or at least not of particles from showers originating in the atmosphere), for we have seen that the cosmic particles of higher penetrating power are subject to the influence of the earth's magnetic field, which proves that they come from a much greater distance than that to which the atmosphere extends. The question to be answered is rather the converse: Is the shower-producing radiation to be considered as a secondary radiation from the hard group of cosmic particles, or should it itself be considered as a primary component of the cosmic radiation?



Whilst admitting that we have not yet sufficient data to decide this question, we shall all the same examine those experimental results which seem most significant in this connection.

The intensity of the shower-producing radiation grows more rapidly with height than the number of cosmic particles. Between Padua (at sea-level) and Asmara (at 2370 m. height), de Benedetti and I found (by the method of coincidences) an increase from 1 to 5 in the number of showers emerging from a lead screen 9 mm. thick, whilst the number of coincidences between three counters with their axes in the same vertical plane (which measures the intensity of the corpuscular radiation) only increased from 1 to 2<sup>(7)</sup>. In a similar way, T. H. Johnson<sup>(29)</sup> finds an increase of 1:6.9 in the frequency of showers and of 1:3.78 in the number of particles, between sea-level and 4250 m. altitude.

Other experiments confirm these results, though in a less direct manner. It follows in fact from our experiments at Eritrea (as I recalled just now) that the intensity of the soft group increases with altitude, relatively to that of the hard group; and the beautiful experiments of Compton and Stephenson in a balloon<sup>(30)</sup>, using an ionization chamber, seem to show the same thing (though they are not so easy to interpret, as the ionization chamber responds to the particles produced in the screen as well as to those passing through it).

Finally, Stevenson and Johnson<sup>(31)</sup> state that the barometric effect (i.e. the diminution of intensity associated with an increase in atmospheric pressure) is more noticeable for the shower-producing radiation than for the corpuscular radiation: this is evidently related to the more rapid variation with altitude. These results would make us incline towards the second hypothesis, which pictures the shower-producing radiation as independent of the primary corpuscular radiation. (I ought to point out, however, that the experiments of Gilbert<sup>(32)</sup> are in disagreement with all the preceding, for they give an increase of the showers with height, proportional to the intensity of the corpuscular radiation; the reason for this disagreement has not yet been cleared up.)

We have seen (figure 4) that the curve connecting the frequency of the showers with the thickness of the lead screen from which they emerge, descends very rapidly just after the maximum. But afterwards the fall becomes extremely slow; Ackermann<sup>(33)</sup> and Hummel<sup>(34)</sup> at Göttingen, and later Drigo in my laboratory<sup>(35)</sup> have even shown that at about 10 cm. the curve turns up again, giving a not very pronounced maximum at about 18 cm.

These results testify to a complexity in the particles of the showers, which seem to be divided into two groups of different range. As for the shower-producing radiation, the form of the curve obtained at sea-level shows, in every case, that its intensity at first diminishes rapidly as the screen thickness increases, and then after several centimetres of lead, becomes almost stationary.

Such a variation of intensity would be explained naturally, if we could suppose that the shower-producing radiation was a secondary radiation from the hard cosmic particles (first hypothesis), and that the intensity of the secondary radiation in equilibrium with a given intensity of primary radiation was greater in air than in lead;

the diminution of intensity in the first few centimetres of lead would then be due to the transition from the condition of equilibrium characteristic of air to that characteristic of lead.

If, on the other hand, the shower-producing radiation is itself a primary radiation (second hypothesis), we must conclude that at sea-level this radiation is composed of two groups of rays of different penetrating power, of which the softer is entirely absorbed by a few centimetres of lead.

I hope that it will be possible to decide between the two hypotheses on the origin of the shower-producing radiation, by further experiments at different heights above sea-level, and under layers of water of different thicknesses.

*Appendix added October 1934*

De Benedetti and I have recently measured at three different heights above sea-level—40 m. (756 mm. Hg), 1350 m. (642 mm. Hg) and 2760 m. (538 mm. Hg)—the intensities  $I_p$  and  $I_s$  of the primary and secondary corpuscular radiation, as well as the frequency  $I_\Delta$  of those secondary processes occurring in a lead screen 9 mm. thick which lead to the simultaneous emission from the screen of groups of two or more particles.

The experiments were carried out by the method of coincidences between three counters, and the upper half of figure 5 shows the different arrangements.  $I_p$  is measured by the number of coincidences observed with arrangement *b*, i.e. with the three counters in a vertical line and with 8 cm. of lead between them.  $I_s$  is measured by the difference between the number of coincidences observed with *a* and with *b*. Finally  $I_\Delta$  is measured by the difference between the number of coincidences observed with *d* and with *c* (the number of the latter is approximately one-tenth of the number of coincidences observed with *d*).

The results are shown below:

Altitude (m.)	Coincidences per minute		
	$I_p$	$I_s$	$I_\Delta$
40	1.19	0.47	0.97
1350	1.68	0.97	1.63
2760	1.85	1.61	2.79

These results, together with the relative errors, are shown in the lower part of figure 5,  $I_p$  being taken as unity in each of the three positions.

It will be seen that the number of secondary particles originating in the air, as well as the frequency of the secondary phenomena having their origin in the lead, increase much more rapidly than the number of primary particles as the altitude increases. Whereas at sea-level the ionization due to secondary particles is only 40 per cent of that due to primary particles, it is nearly 90 per cent at 2760 m.; higher still, we may expect that the greater part of the ionization will be due to secondary particles.

These results are in accord with those which we found at Eritrea last year; they are, however, more complete and more accurate, for the observations at different heights were carried out under very light roofs or in a tent, whereas last year the

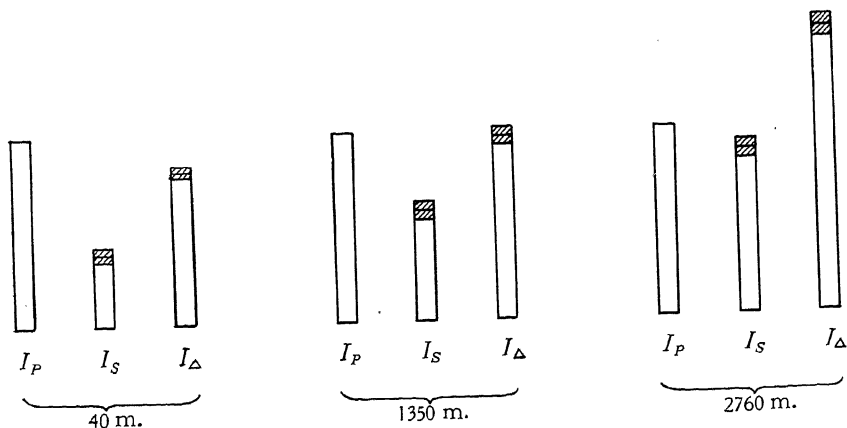
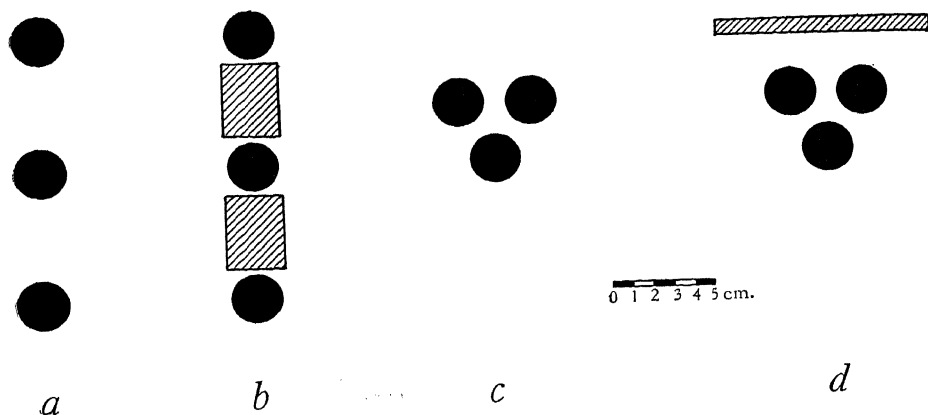


Figure 5.

observations at sea-level were carried out in a laboratory (which explains the imperfect quantitative agreement).

It seems to me that the aggregate of facts known at present as to the number of secondary particles at different heights and their angular distribution is difficult to explain, if it is assumed that all the secondary particles are originated (directly or indirectly) by the primary particles forming the hard group. We are forced to

assume the existence of another component of the primary radiation, in addition to these particles, which is more rapidly absorbed in the atmosphere and which exerts its ionizing action chiefly through the intermediary of the secondary particles which it produces in matter. The production of secondary particles must thus represent the chief means by which this radiation is absorbed.

It is, moreover, well known that the primary cosmic radiation contains some relatively feebly penetrating rays which cannot be of the nature either of low energy electrons or protons, since either would be deflected away by the earth's magnetic field. I believe that this easily absorbed part of the primary cosmic radiation is composed of those rays which produce the secondary particles.

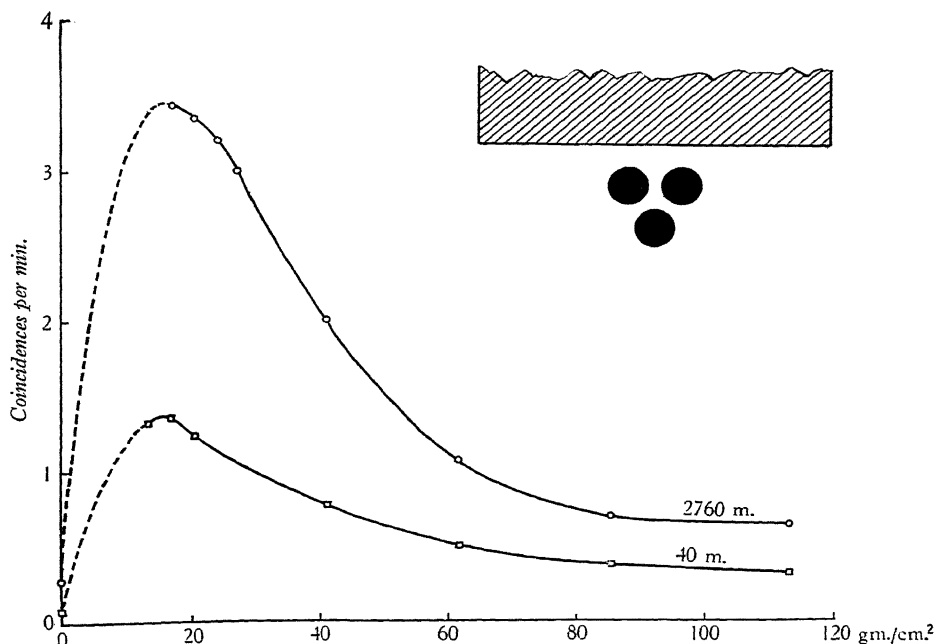


Figure 6.

In other words, as we rise in the atmosphere the absorption coefficient of the total cosmic radiation increases considerably at the same time as its capacity for producing secondary rays increases; these two facts are doubtless connected with each other, i.e. the cause of the feeble penetrating power observed in the rays in the upper atmosphere (whether these are charged particles or not) must be sought in the large number of secondary rays to which they give rise.

As to the way in which the secondary particles are produced, I think that in the upper atmosphere it does not differ from the process at sea-level, where we know that the majority of the particles occur in showers, and that the immediate cause of the showers is the peculiar radiation known as "shower-producing radiation." In fact, de Benedetti and I have measured the frequency of triple coincidences between

three counters in a triangle for different thicknesses of the lead screen placed over them, both at 2760 m. and at sea level; the two curves we obtained (Fig. 6) are quite similar in form, and in particular they both show the rapid fall after the maximum which proves that the showers are not produced by cosmic particles from the hard group, but by a considerably softer radiation.

If the majority of the secondary particles are particles from showers, then the rapid increase of secondary particles with height (as well as the increase of frequency of the triple coincidences when the counters form a triangle) proves that the intensity of the shower-producing radiation also increases with height more rapidly than cosmic particles of the hard group; this is not in agreement with the hypothesis that the shower-producing radiation is produced in its turn by these particles in matter. We should rather be led to suppose that the shower-producing radiation itself forms part of the primary cosmic radiation, and in fact constitutes precisely that soft component of which I have just spoken. From the diminution in the number of triple coincidences between three counters in a triangle that is observed between 2760 m. and 40 m. (as well as that of the number of secondary particles), its absorption coefficient per gm./cm<sup>2</sup> in air can be calculated; the value found is about ten times smaller than that of the same radiation in lead (which can be calculated from the curve giving the showers as a function of screen thickness); this is just what we must expect if the effective cross-section of the different atoms for shower-producing radiation is proportional to the square of the atomic number.

Whilst considering the existence of a primary shower-producing radiation as extremely probable, I do not wish in any way to assert that a secondary shower-producing radiation may not be present; the phenomenon of showers is in any case so complex that it would not be surprising if there are several sorts of showers, produced by rays of different kinds.

#### REFERENCES

- (1) W. BOTHE and W. KOLHÖRSTER. *Z. f. Phys.* **56**, 751 (1929).
- (2) B. ROSSI. *Naturwiss.* **20**, 65 (1932); *Z. f. Phys.* **82**, 151 (1933).
- (3) R. A. MILLIKAN. *Phys. Rev.* **43**, 661 (1933). (See also (20) below.)
- (4) B. ROSSI. *Phys. Z.* **33**, 304 (1932).
- (5) P. M. S. BLACKETT and G. P. S. OCCHIALINI. *Proc. Roy. Soc.* **139**, 699 (1933).
- (6) B. ROSSI and G. BOTTECHIA. *Ricerca Scient.* **5**, 1, 171 (1934).
- (7) B. ROSSI. *Phys. Rev.* **45**, 212 (1934); B. ROSSI and S. DE BENEDETTI. *Ricerca Scient.* **5**, 1, 594 (1934).
- (8) B. ROSSI. *Phys. Rev.* **36**, 606 (1930). See also E. FERMI and B. ROSSI. *Rend. Lincei*, **17**, 346 (1933).
- (9) J. CLAY and H. P. BERLAGE. *Naturwiss.* **20**, 687 (1932).
- (10) A. H. COMPTON. *Phys. Rev.* **43**, 387 (1933).
- (11) H. HÖRLIN. *Nature*, **132**, 61 (1933).
- (12) P. AUGER and L. LEPRINCE-RINGUET. *Nature*, **133**, 138 (1934).
- (13) B. ROSSI, I. RANZI and S. DE BENEDETTI. *Ricerca Scient.* **5**, 1, 575 (1934).
- (14) B. ROSSI. *Rend. Lincei*, **13**, 47 (1931); *Nuovo Cim.* **8**, 85 (1931).
- (15) T. H. JOHNSON. *Phys. Rev.* **43**, 834 (1933); **44**, 856 (1933).
- (16) L. ALVAREZ and A. H. COMPTON. *Phys. Rev.* **43**, 835 (1933).
- (17) B. ROSSI. *Ricerca Scient.* **4**, 11, 365 (1933) and **5**, 1, 579 (1934).

- (18) J. CLAY. *Physica*, **1**, 363 (1934).
- (19) C. D. ANDERSON. *Phys. Rev.* **44**, 406 (1933).
- (20) C. D. ANDERSON, R. A. MILLIKAN, S. NEDDERMEYER and W. PICKERING. *Phys. Rev.* **45**, 352 (1934).
- (21) B. ROSSI. *Helv. Phys. Acta*, **4**, 440 (1933).
- (22) W. BOTHE. *Atti del Convegno di Fisica Nucleare*, p. 153 (Rome, 1931).
- (23) B. ROSSI and B. CRINÒ. *Rend. Lincei*, **15**, 741 (1932).
- (24) B. ROSSI. *Nature*, **132**, 173 (1933).
- (25) B. ROSSI. *Rend. Lincei*, **15**, 734 (1932); *Z. f. Phys.* **82**, 151 (1933).
- (26) E. FÜNFER. *Z. f. Phys.* **83**, 92 (1933).
- (27) J. H. SAWYER. *Phys. Rev.* **44**, 241 (1933).
- (28) G. ALOCCO and A. DRIGO. *Ricerca Scient.* **5**, 1, 112 (1934).
- (29) T. H. JOHNSON. *Phys. Rev.* **45**, 569 (1934).
- (30) A. H. COMPTON and R. J. STEPHENSON. *Phys. Rev.* **45**, 441 (1934).
- (31) E. C. STEVENSON and T. H. JOHNSON. *Phys. Rev.* **54**, 758 (1934).
- (32) C. W. GILBERT. *Proc. Roy. Soc.* **144**, 559 (1934).
- (33) M. ACKERMANN. *Naturwiss.* **22**, 169 (1934).
- (34) J. N. HUMMEL. *Naturwiss.* **22**, 170 (1934).
- (35) A. DRIGO. *Ricerca Scient.* **5**, 11, 88 (1934).

## DISCUSSION

Dr G. BERNARDINI. It is not yet settled if the showers associated with cosmic radiation are produced by an ionizing or non-ionizing agency\*. The generating radiation is generally thought to be absorbed† in producing the showers and to have a  $\mu$  of  $0.3 \text{ cm}^{-1}$  compared with a  $\mu$  of  $0.006 \text{ cm}^{-1}$  for the actual penetrating radiation.

In order to throw some light on the nature of the shower-producing radiation, I performed the following experiments‡. I placed three Geiger-Müller tube counters in a vertical plane as seen schematically in figure 1. Between counters I and II was a 7 cm. layer of lead, 7 cm. long and 3.5 cm. wide. Another lead layer equally large and 1.5 cm. thick was placed either between counters II and III or added to the above 7 cm. layer. A valve device registered automatically and simultaneously triple coincidences between I, II, III and double coincidences between I and III.

From earlier results\* it would be expected:

(i) that when both lead slabs (*a*) and (*b*) were between counters I and II, the primary radiation would go through, mainly in equilibrium with the shower-producing radiation, and the actual showers. The composite radiation emerging from the lead would determine an impulse in counter II and in counter III.

(ii) When lead (*b*) was between counters II and III in (*a*) the shower-producing radiation would be in equilibrium and pass through counter II, and finally find itself in equilibrium with the showers produced in (*b*). Thus, if the shower-producing radiation is not ionizing, it would occur at times that a systematic coincidence would be recorded while the middle counter was not affected. That is to say, one would expect a double coincidence without the corresponding triple one, and the ratio

\* See, for example, Blackett and Occhialini, *Proc. Roy. Soc. A*, **139**, 669 (1933); T. H. Johnson, *Phys. Rev.* **45**, 569 (1934), and others.

† B. Rossi, *Z. f. Phys.* **82**, 151 (1933); C. W. Gilbert, *Proc. Roy. Soc. A*, **144**, 853 (1934); E. Fünfer, *Z. f. Phys.* **83**, 93 (1933).

‡ See also G. Bernardini, *Rivista scientifica*, V, 1, 9 (1910).

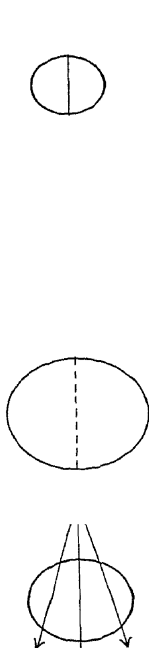


Figure 1.

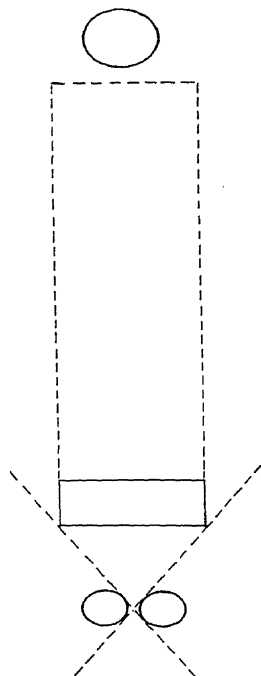


Figure 2.

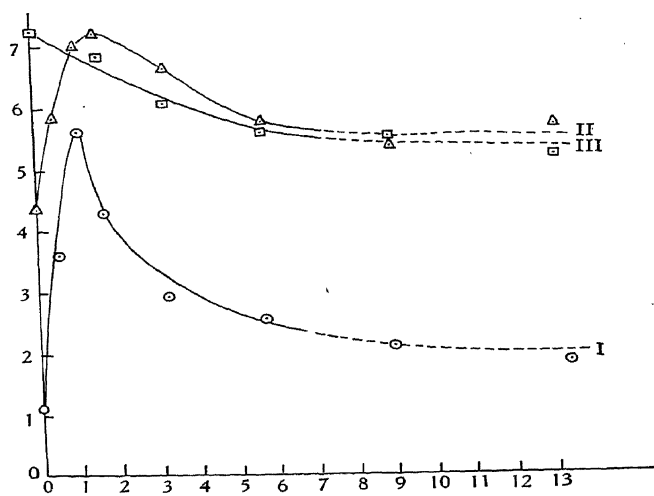


Figure 3.

triple/double should be smaller than in case (i) when all the lead is above the second counter.

The results are given below:

	No lead between the counters			All lead above counter II			7 cm. lead between counters I and II 1.5 cm. lead between counters II and III		
	$t$	$n_3$	$n_2$	$t$	$n_3$	$n_2$	$t$	$n_3$	$n_2$
	3068	4354	5558	2580	2921	3756	2640	3061	3927
$\frac{n_3}{n_2}$	$78.24 \pm 0.55$			$77.8 \pm 0.7$			$77.9 \pm 0.7$		

Later, a complete series of triple coincidences was registered between counter I and two lower counters placed below for different interposed lead layers (see figure 2). At the same time, the increased number of coincidences between the two lower counters was independently recorded. As is seen in figure 2, the two counters were placed in such a manner that a particle coming from the lead above could not affect both. The results, of a preliminary nature, are given in figure 3, curves I and II, whilst III gives the double coincidences when the lower are connected.

Lead thickness in cm.	0	0.55	1.1	1.65	3.3	5.7	9	13.4
Time in min.	1400	1390	1430	1410	1353	1620	1440	1670
Double coincidences per min.	0.876	1.182	1.398	1.432	1.311	1.143	1.065	1.120
Triple coincidences per min.	0.011	0.036	0.056	0.043	0.029	0.025	0.021	0.018

Notwithstanding the fact that the experimental error is rather serious, it is obvious that curve I could not be explained by the hypothesis that the non-ionizing shower-producing radiation is itself produced by the primary ionizing corpuscular radiation.

It is still impossible to decide definitely if the shower-producing radiation is or is not ionizing. The results are not easily reconcilable with the hypothesis of a secondary non-ionizing agent. In this last case we must either admit that most showers are constituted also of particles ejected backwards, or that the generation of two or more ionizing particles by one incident ionizing particle, in these particular experimental conditions, is more frequent than in the experiments cited\*.

Experiments which are not completed seem to show that the most important agent in the production of showers is a non-ionizing radiation, which is quite independent of the primary corpuscular radiation†. As we have shown above, there are also processes where very few particles produced by a corpuscular radiation impact are emitted‡.

\* B. Rossi, *Z. f. Phys.* **82**, 151 (1933); C. W. Gilbert, *Proc. Roy. Soc.* **144**, 853 (1934); E. Fünfer, *Z. f. Phys.* **83**, 93 (1933).

† Cf. paper by Rossi, this volume, p. 233.

‡ Cf. G. Bernardini and D. Bocciarelli, *Rivista Scientifica* **2**, 464 (1934).



Dr H. A. BETHE. The experiments of Anderson and Neddermeyer on the passage of cosmic-ray electrons through lead are extremely valuable for theoretical physics. They show that a large fraction of the energy loss by electrons in the energy range round  $10^8$  volts is due to emission of  $\gamma$ -radiation rather than to collisions, but still the radiative energy loss seems far smaller than that predicted by theory. Thus the quantum theory apparently goes wrong for energies of about  $10^8$  volts, and it would be of special value for any future quantum electrodynamics to know exactly at which energy the present theory begins to fail, in other words to have much more experimental data on the energy loss of fast electrons (energy  $10^7$  to  $5 \times 10^8$  volts) passing through matter.

Dr C. W. GILBERT. Prof. Blackett and I have made experiments at an altitude of  $10.7$  km. on the angular distribution of the cosmic radiation about the vertical. We used two independent sets of Geiger counters recording triple coincidences, the counters being mounted in lead so that to cause a coincidence a particle must traverse about  $5$  cm. of lead.

We have so far obtained two results:

(1) The shapes of the angular distribution curves at  $10.7$  km. and at sea-level are the same within the limits of the experimental error.

(2) The intensity at  $10.7$  km. is about  $7$  times that at sea-level.

Other workers using unshielded apparatus find about a thirty-fold increase between  $10.7$  km. and sea-level. Our low value is due to the absorption of the soft radiation and is in agreement with that of other workers using shielded apparatus.

We should like to express our appreciation to the Air Ministry for the loan of the aeroplane in which the experiments were carried out.

Prof. V. POSEJPAL. In discussing cosmic radiation, may I be allowed to call attention to the relevancy of my recent experiments on the formation of hydrogen in a vacuum? These experiments\*, which I am continuing, have clearly shown the formation of hydrogen on fine wire electrodes in a high vacuum, using large differences of potential. In other words, I find the formation of hydrogen *in vacuo* under the well-known conditions of the auto-electronic discharge.

The interest lies on the one hand in the view-point which led me to undertake these observations, and on the other, in the agreement between the measured results and the theoretical predictions. I assume† that the ether is composed of atoms with no inertial mass and of atomic number zero, the nucleus consisting of a proton and an electron. Since the discovery of the positron leads us to accept the possible existence of particles analogous to the proton and the electron but of opposite sign, it follows that, in principle, the ether atoms may be formed by the aggregation of any pair of these particles, if one is positive and the other negative.

We may assume that the ether has been formed from the free particles with the production of photons. Conversely, these photons can lead to the separation of charged particles inside the ethereal atoms, so that the ether can be the seat of

\* *Comptes Rendus*, **198**, 59 (1934); **199**, 186 (1934).

† *J. d. Phys.* **3**, 390 (1932).

incessant play of disappearance of inert mass in favour of the photons; and vice versa the photons will disappear with the formation of inert matter by materialization of ether. Let us consider particularly ethereal proton-electron atoms. The laws of conservation of energy, charge and momentum predict that the proton and electron at rest will produce two oppositely directed photons of quanta  $h\nu = \frac{1}{2}m_Hc^2$  when they unite *in vacuo* to form an ether atom. The converse process, also occurring *in vacuo*, would take place when two photons of similar size and direction met in the ether atom considered. In the absence of an external electric field, the two particles so formed would reunite immediately if the energy  $h\nu$  of the colliding photons were equal to, or even a little less than,  $\frac{1}{2}m_Hc^2$ , as would usually be the case. But in a sufficiently intense field, the separation could be complete, and this is what I find in my experiments. In a vacuum, i.e. in free ether, we may assume that the number of proton-electron ether atoms is very large, so that the photons  $\frac{1}{2}m_Hc^2$  form an intense, and obviously highly penetrating, cosmic radiation. Our experiments on the formation of hydrogen in a vacuum can only be the disintegration of proton-electron nuclei of atomic number zero by this cosmic radiation, in the presence of an intense electric field.

Prof. E. REGENER. I should like to give an account of the work of certain of my pupils.

(1) Hoerlin measured the cosmic-ray intensity on mountains at various altitudes in Peru (magnetic latitude  $2^\circ$  N.) and in Switzerland (magnetic latitude  $49^\circ$  N.). The greatest height in Peru was 6100 m. and in Switzerland (Mönchgipfel) 4100 m.

The measurements were made with a spherical ionization chamber of Regener's pattern, filled with  $\text{CO}_2$  at 7.5 atmospheres.

Two sets of observations were made. For the first set the chamber was completely surrounded by an iron shield 10 cm. thick, and for the second the upper half of the shield was removed. The results are shown plotted in figure 1. Curves *A* refer to the first set, curves *B* to the second set.

The latitude effect between  $2^\circ$  N. and  $49^\circ$  N. is seen to be:

Shield	Sea-level	4100 m.
Closed	12 per cent	28 per cent
Open	13 „	36 „

For a more detailed report see *Phys. Z.* **35**, 793 (1934).

(2) Working with Auer, I have measured cosmic-ray intensity at different altitudes by means of pilot balloons fitted with open ionization chambers, in which the pressure was therefore always the same as the pressure outside.

The advantage of this over the constant-pressure ionization chamber lies chiefly in that the increase of cosmic-ray intensity with height is to a certain extent compensated by the diminution in pressure, in consequence of which the ionization current at altitudes of 25 to 30 km. is only about 5 times greater than at sea-level.

With a constant-pressure ionization chamber, however, the current increases in the ratio of 150 to 1, which renders it impossible to obtain sufficient accuracy when the same apparatus is used throughout the range.

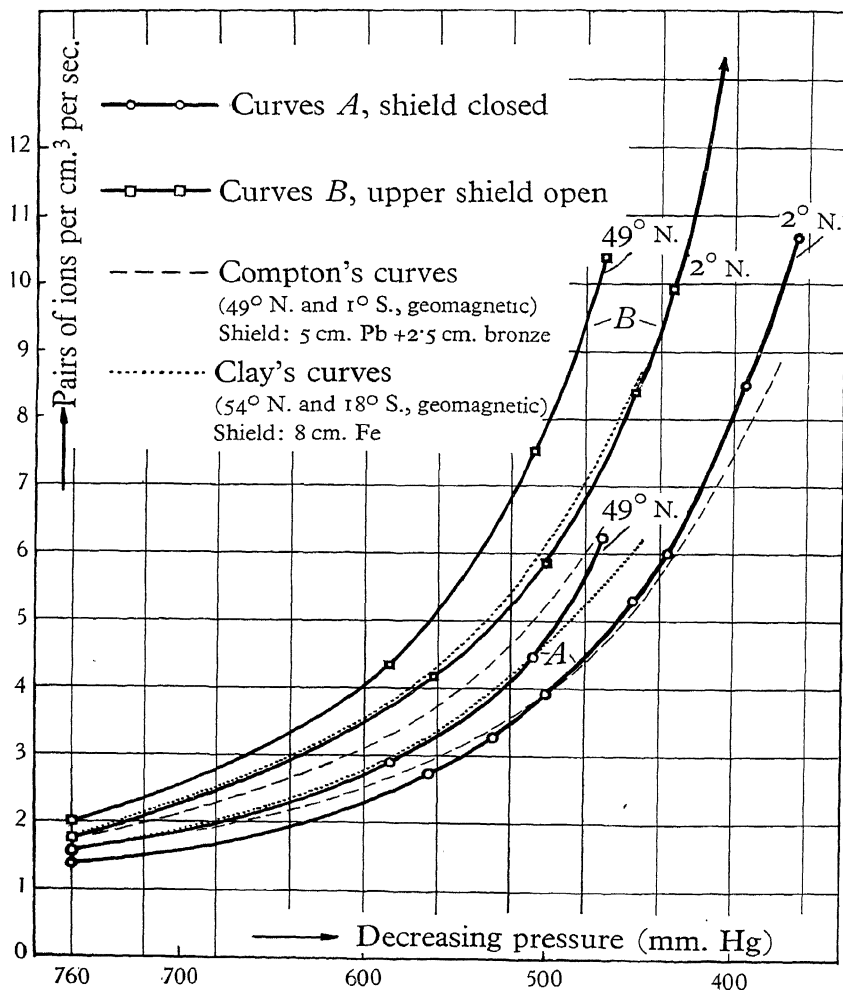


Figure 1.

Four ascents were made, three with a 105 litre chamber and one with a 194 litre chamber, shown in figure 2. The experimental results are given in figure 3, where the ionization is plotted against the superincumbent mass of air. All four curves are similar, exhibiting a maximum in the neighbourhood of a pressure of 140 mm. of mercury. This corresponds to the height at which cosmic-ray intensity becomes

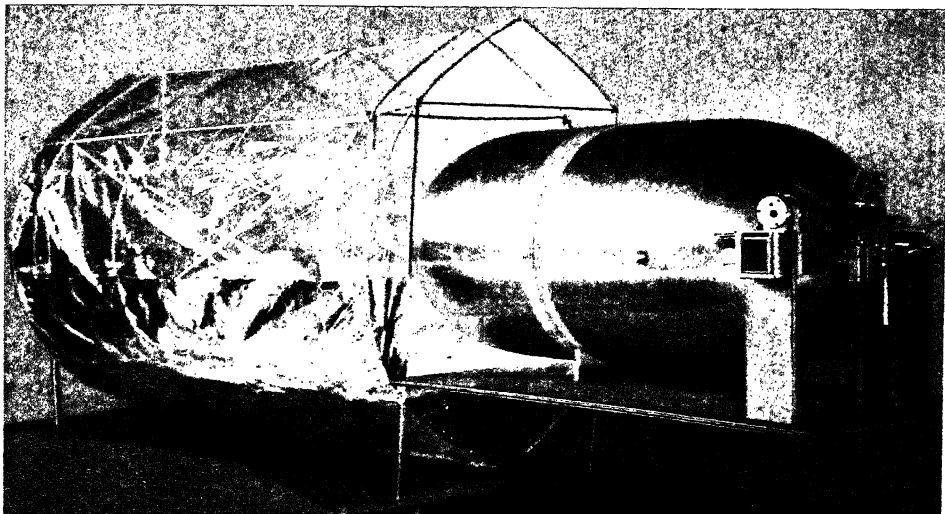


Figure 2.

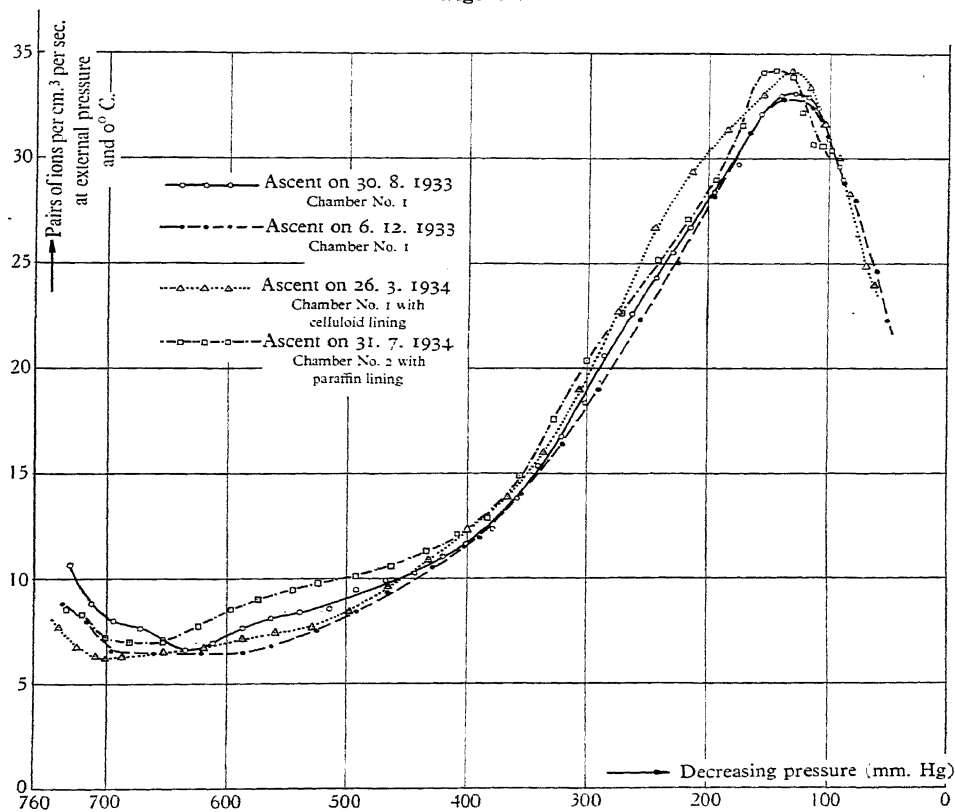


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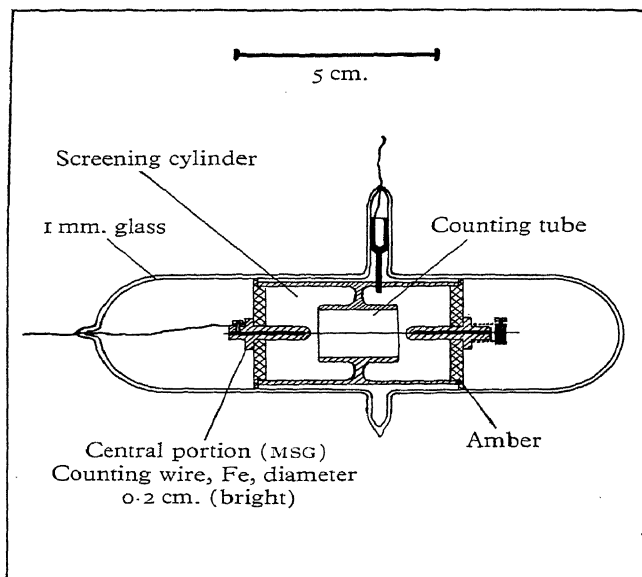


Figure 4.

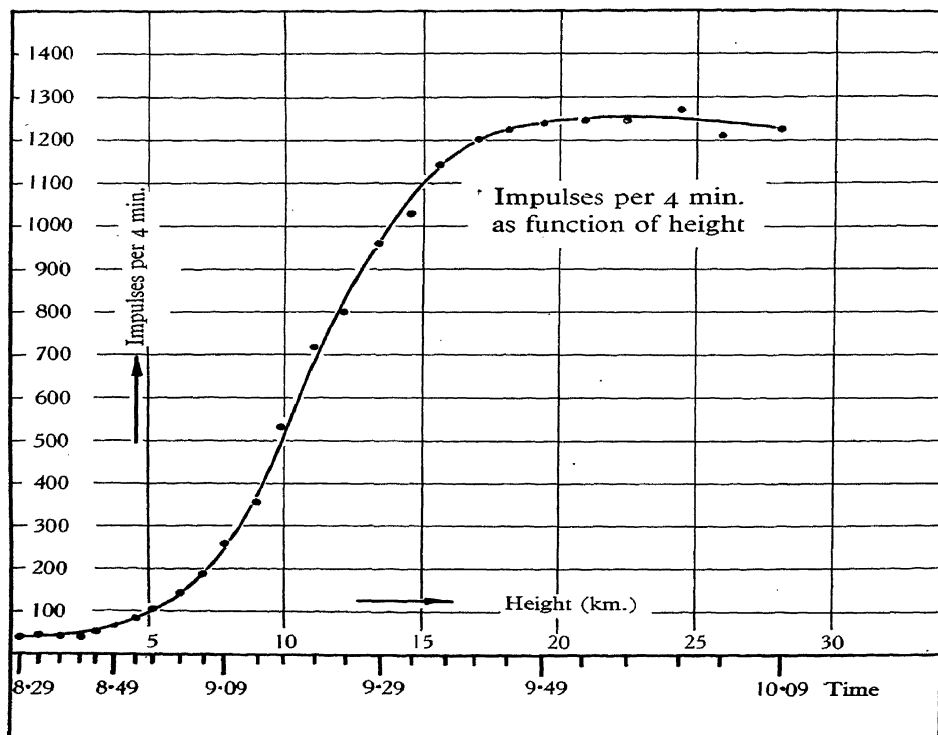


Figure 5.

approximately constant, so that the diminution of pressure with altitude is no longer compensated.

For two ascents the ionization chamber was coated inside with a thin layer of paraffin wax or of celluloid, with a view to detecting neutrons, in case any were present, but, to the accuracy of the measurements, the result was negative in each

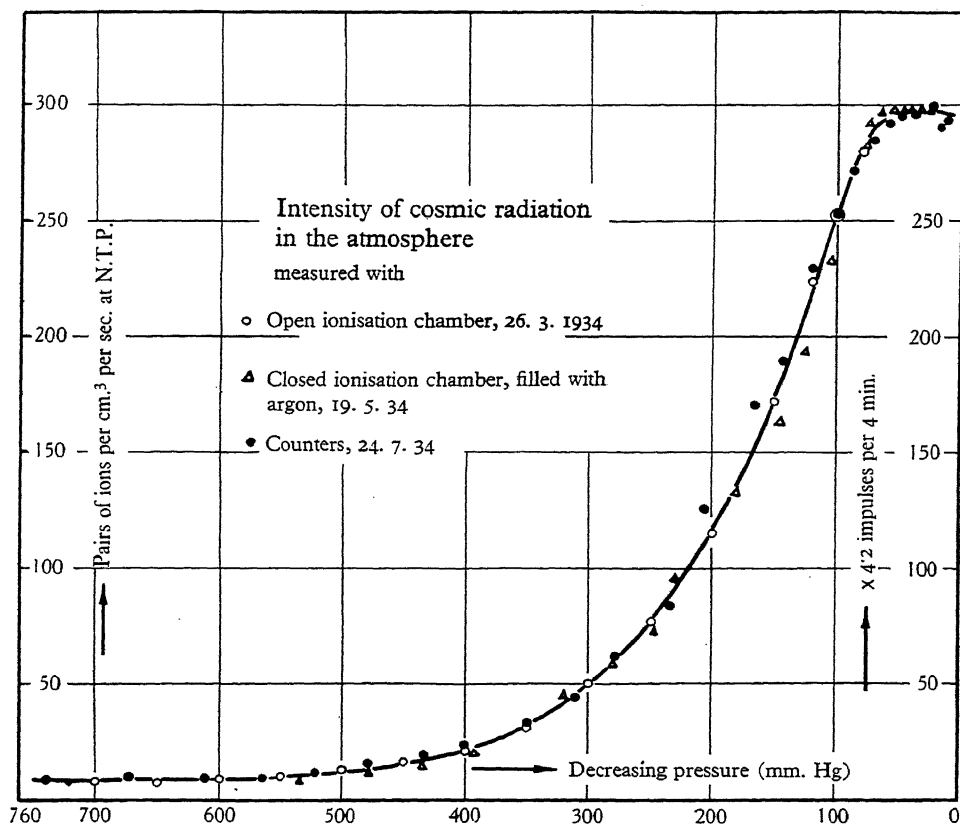


Figure 6.

case. Neutrons cannot, therefore, be an important constituent of cosmic radiation at high altitudes.

For a more detailed report see *Phys. Z.* **35**, 784 (1934).

(3) With Pfozter I have measured the cosmic-ray intensity at altitudes up to 28 km. with Geiger-Müller counters, carried by four pilot balloons. Figure 4 shows the counter, sealed in a glass tube. Its length is such that the sensitivity is the same for all directions. The high-tension battery of 1200 volts weighs only 1.2 kg. The indications of pressure and temperature and those of the counting apparatus were photographed on a rotating plate every four minutes. The variations of tempera-

ture were reduced to a few degrees by means of cellophane, an important matter if variations are to be avoided in the e.m.f. of the batteries.

Figure 5 shows the increase in the number of impulses with altitude.

Figure 6 shows the number of deflexions plotted against the pressure, and also the ionization, measured with a constant-pressure chamber. It is seen that the two curves run together, showing that the mean ionizing power of cosmic particles does not change appreciably with altitude.

For a more detailed report see *Phys. Z.* 35, 779 (1934).

Prof. D. SKOBEŁTZYN. An important fact is brought to light by the experiments of Anderson and Neddermeyer. It is that the passage through sheets of lead and carbon of "ultra- $\beta$ " particles, i.e. particles whose energy is of the order of hundreds of millions of volts, is not accompanied by appreciable secondary emission of positrons.

On the other hand, E. Stepanowa and I, working with ordinary  $\beta$ -rays (those of radium B + C, with energies below 3 million volts) were able to detect positron emission. Those positrons are certainly produced, with a relatively high efficiency,

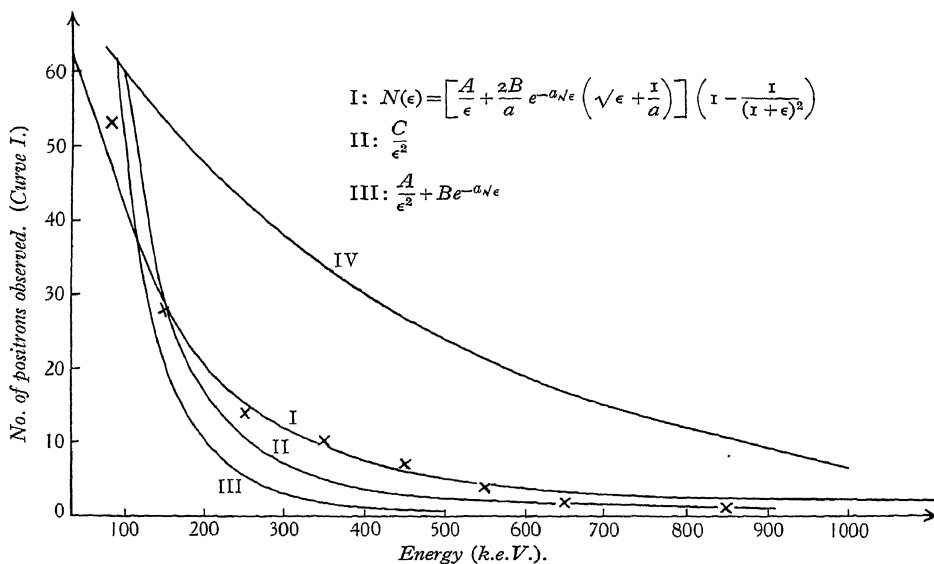


Figure 7.

during the collisions of the  $\beta$ -particles. Under favourable circumstances it is possible to detect one positron for every 25 to 30  $\beta$ -particles emitted under ordinary conditions from Ra B + C, with energies above the critical value of 1 million volts.

The method used by us is very simple. A lead tube containing a very weak radioactive source is placed inside a Wilson chamber provided with a magnetic field. The tube is pierced with a small hole through which a beam of  $\beta$ -rays emerges, and in front of which layers of various materials can be placed. Some of

the photographs show, in addition to the tracks of the primary  $\beta$ -rays, other electron tracks starting from the screen in front of the hole, and these trajectories are deflected in a direction corresponding to a positive charge. It is as easy to prove that the effect cannot be due to  $\gamma$ -rays as it is to distinguish between the secondary positrons and those which might conceivably be emitted by the radioactive source itself.

A study of the phenomenon yielded certain results to which I should like to draw attention.

The diagram, in which the intensity of emission is plotted against the energy of the particles, shows the distribution of the velocities of the positrons. Curve I, which gives the actual observed distribution, shows that the positrons are relatively slow, mostly corresponding to energies of the order of 100 kilovolts; it also shows—and this is an altogether characteristic property—a rapid decrease in the high-speed region. The distribution of the primary emission is given by curve IV.

The actual observed distribution is, however, strongly influenced by the resistance offered to the motion of the positrons by the substance in which they are produced. By introducing various simplifications, it is possible to deduce the initial speed distribution. This can be represented by curve II or curve III, according to the assumptions made in the calculations.

The law connecting the intensity of emission and the energy of the particles is certainly very simple. The result in curve II, viz. that the intensity of emission is inversely proportional to the square of the energy, is probably correct. Curve I, which gives the result of the direct statistical study, can itself be expressed by the relatively simple formula

$$N(\epsilon) = \left\{ \frac{A}{\epsilon} + \frac{2B}{a} e^{-a\sqrt{\epsilon}} \left( \sqrt{\epsilon + \frac{1}{a}} \right) \left\{ 1 - \frac{1}{(\epsilon + 1)^2} \right\} \right\},$$

in which  $\epsilon$  is equal to  $E/mc^2$ ,  $E$  being the kinetic energy.

From the statistical data obtained, it is possible to evaluate the mean effective cross-section for primary particles with energies between 1 and 3 million volts. When the mean energy of the secondary positrons is taken into account, the value obtained for lead is of the order of  $10^{-22}$  sq. cm., and the effective area per atom appears to be proportional to the atomic number. The important point is that this value of the effective area is about a hundred times greater than for photoelectric emission of positrons by photons of the same energy. Such a high effective area appears wholly incompatible with theoretical results.

In conclusion, the facts of the case can be stated thus: the Wilson cloud-chamber provides a reliable means of establishing secondary positron emission by  $\beta$ -rays, and for studying the phenomenon, but it seems impossible to reconcile experimental results with theoretical predictions.



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# International Conference on Physics

London 1934

A JOINT CONFERENCE ORGANIZED  
BY THE INTERNATIONAL UNION OF PURE  
AND APPLIED PHYSICS

AND  
THE PHYSICAL SOCIETY

## PAPERS & DISCUSSIONS

In two volumes

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# CONTENTS

## VOLUME II

	PAGE
1. PREFACE	v
2. OPENING SURVEY	<i>Sir William Bragg</i>
3. THE STRUCTURE OF MOLECULES AND OF THE IDEAL LATTICE	
Aromatic and Unsaturated Molecules: Contributions to the Problem of their Constitution and Properties	<i>E. Hückel</i> 9
Description of the Binding Forces in Molecules and Crystal Lattices on Quantum Theory	<i>F. Hund</i> 36
Atomic Distances in Organic Compounds by X-ray Analysis	<i>J. M. Robertson</i> 46
Discussion on the Structure of Molecules and of the Ideal Lattice	<i>J. D. Bernal,</i> <i>P. P. Ewald, A. Müller,</i> <i>J. C. Slater</i> 50
4. THE DEVIATIONS OF REAL CRYSTALS FROM THE IDEAL LATTICE STRUCTURE	
The Mosaic Texture of Rock Salt	<i>P. P. Ewald and</i> <i>M. Renninger</i> 57
Experimental Evidences of Group Phenomena in the Solid Metallic State	<i>A. Goetz</i> 62
On the Cause of the Low Value of Mechanical Strength	<i>A. Joffé</i> 72
On the Mechanism of Brittle Rupture	<i>A. Joffé</i> 77
The Rupture of Plastic Crystals	<i>E. Orowan</i> 81
The Structure-Sensitive Properties of Salt Crystals	<i>A. Smekal</i> 93
Discussion on the Deviations of Real Crystals from the Ideal Lattice Structure	109
<i>C. H. Desch; E. N. da C. Andrade; Sir William Bragg; G. Antonoff; J. D. Bernal; J. Brentano; W. G. Burgers; F. Canac; J. A. Darbyshire; G. I. Finch; R. H. Fowler; Sir R. Hadfield; A. Joffé; E. Orowan; B. Lockspeiser; Sir William Bragg; E. Orowan; A. Smekal; Sir R. Robertson; A. Smekal; A. Joffé; E. Orowan; C. F. Tipper (Elam); A. E. H. Tutton.</i>	



	PAGE
5. PLASTICITY AND STRAIN HARDENING IN CRYSTALS	
Shear Hardening and Recrystallization of Aluminium <i>W. G. Burgers</i>	139
Single Crystals	
On Plasticity, Crystallographic and Non-Crystallo- <i>E. Schmid</i>	161
graphic	
Discussion on Plasticity and Strain Hardening in	171
Crystals	
<i>H. J. Gough; E. N. da C. Andrade; W. F. Berg; Sir R. Hadfield; A. Smekal;</i>	
<i>E. Schmid.</i>	

# CONTENTS

## VOLUME II

	PAGE
1. PREFACE	v
2. OPENING SURVEY	<i>Sir William Bragg</i>
3. THE STRUCTURE OF MOLECULES AND OF THE IDEAL LATTICE	
Aromatic and Unsaturated Molecules: Contributions to the Problem of their Constitution and Properties	<i>E. Hückel</i> 9
Description of the Binding Forces in Molecules and Crystal Lattices on Quantum Theory	<i>F. Hund</i> 36
Atomic Distances in Organic Compounds by X-ray Analysis	<i>J. M. Robertson</i> 46
Discussion on the Structure of Molecules and of the Ideal Lattice	<i>J. D. Bernal,</i> <i>P. P. Ewald, A. Müller,</i> <i>J. C. Slater</i> 50
4. THE DEVIATIONS OF REAL CRYSTALS FROM THE IDEAL LATTICE STRUCTURE	
The Mosaic Texture of Rock Salt	<i>P. P. Ewald and</i> <i>M. Renninger</i> 57
Experimental Evidences of Group Phenomena in the Solid Metallic State	<i>A. Goetz</i> 62
On the Cause of the Low Value of Mechanical Strength	<i>A. Joffé</i> 72
On the Mechanism of Brittle Rupture	<i>A. Joffé</i> 77
The Rupture of Plastic Crystals	<i>E. Orowan</i> 81
The Structure-Sensitive Properties of Salt Crystals	<i>A. Smekal</i> 93
Discussion on the Deviations of Real Crystals from the Ideal Lattice Structure	109
<i>C. H. Desch; E. N. da C. Andrade; Sir William Bragg; G. Antonoff; J. D. Bernal; J. Brentano; W. G. Burgers; F. Canac; J. A. Darbyshire; G. I. Finch; R. H. Fowler; Sir R. Hadfield; A. Joffé; E. Orowan; B. Lockspeiser; Sir William Bragg; E. Orowan; A. Smekal; Sir R. Robertson; A. Smekal; A. Joffé; E. Orowan; C. F. Tipper (Elam); A. E. H. Tutton.</i>	

	PAGE
5. PLASTICITY AND STRAIN HARDENING IN CRYSTALS	
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On Plasticity, Crystallographic and Non-Crystallo- <i>E. Schmid</i>	161
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# OPENING SURVEY

By SIR W. H. BRAGG, O.M., F.R.S.

THE importance and interest of those phenomena of the Solid State which are to be considered at this meeting of the International Union of Physics are most agreeably emphasized by the largeness of the attendance and by the presence of so many recognized authorities. Especially may we congratulate ourselves on the fact that well-known investigators have come to us from many countries, from America in the West which gives us our President Dr Millikan to Russia in the East which sends us representatives of the distinguished staff directed by Dr Joffé in Leningrad.

This is by no means the first conference that has discussed the problems of the Solid State. At the root of all physical and chemical advance lies the urgent need for fuller understanding of the forces that bind atoms and molecules together. In recent years we have acquired new powers of examining the structure of the solid and of observing the action of the atomic forces under new conditions. The consequent growth of knowledge has been rapid, and it is not surprising that successive Conferences have met to discuss it and to co-ordinate it. The promoters of this Conference have believed that there is again the need and the opportunity for a further review: their belief is already fully justified by the excellence of the papers that have been prepared and are now in our hands.

It has been thought well to arrange the subjects for discussion into two groups. In the one, consideration will be given to certain physical phenomena which are characteristic of the Solid State: the other will consider the efforts to apply mathematical analysis to observed facts. I have been asked to make a preliminary statement which will explain in general terms the significance of the advances that are being made in each of these directions.

Twenty years ago it was discovered that the arrangement of the atoms in a crystal might be examined by the use of X-rays. The new method was eagerly applied to the determination of crystalline structures of all kinds. One of the most striking facts revealed in the course of the search was the wide prevalence of the crystalline structure: it had not been previously realized that the regularity of arrangement characteristic of

the crystal is a normal condition of the solid body. The X-rays had something to tell of the constitution of substances of all kinds: not merely of those that are obviously crystalline, nor only of those that under special circumstances look to be crystalline, such as the metals, but also of such apparently amorphous substances as woods and vegetable fibres generally, of the materials of the living world, the cell wall, nerve and muscle, hair and wool.

During these twenty years of intensive research certain very important facts have become gradually more clear. One of them is the extreme precision with which the crystal structure can be measured, and a second is the constancy of the structural dimensions of the crystal pattern no matter what the origin of the crystal may be nor in what way it may have been treated. For example, measurements of the length of the cubic element of the rocksalt structure made by different investigators on various specimens agree to less than one part in a thousand. Nor does the presence of impurities invalidate the measurements. It is naturally a very great pleasure to the experimenter to find that the crystal responds to every effort that he makes to improve the accuracy of his measurements. And of course it is also gratifying to see in the details of the structures that are revealed, the origins of many of the phenomena which the crystals themselves display, such as the manifold yet invariable details of form, the existence of cleavage and the position of the cleavage plane, the hardness of the diamond, the fibrous appearance of asbestos and so forth. The exactness of the X-ray determinations forms a solid ground on which to found further enquiries.

Yet the very exactness and universality of the X-ray results are evidence of their insufficiency. There are phenomena of the solid state which they cannot of themselves explain. The strength and rigidity of a crystal may vary enormously while there is no change in the X-ray indications and therefore none in the geometric structure of the crystal. There are other properties that display a similar independence in greater or less degree, such as the conductivities for heat and electricity, or the coloration under the action of radiation. Clearly the perfect geometric structure is not the only determining factor in the behaviour of the crystal.

This point of view has been clearly set forth by Smekal: and the promoters of this conference have been gratified by his consent to attend and to state his arguments in a comprehensive paper. He has long insisted on a distinction to be drawn between what may be defined as "sensitive" and "insensitive" effects. The latter include all those effects

which are functions of the composition of the crystal itself, and of little else, such as the structure in all its details revealed by X-rays. The former, such as hardness, conductivity and so on may vary widely, being sensitive to external influences and the past history of the crystal. Certain aspects of this question are considered in a very interesting paper by Prof. Ewald and Dr Renninger.

It is perhaps well to pause at this point in order to realize the meaning and purpose of such considerations as these, and of the researches to which they lead. All our investigations of the solid bodies of every form, animal, vegetable and mineral, have as a principal aim the connexion between the properties of the body on the one hand and its composition and architecture on the other. Some of these properties are directly dependent on the few atoms of the unit cell in the crystal. Their arrangement determines the behaviour of the body as a whole. But there are other properties which depend on atomic relations which are not fully developed within the cell: a larger field is required. The action of the atomic forces in groups of hundreds or thousands or tens of thousands of atoms must be considered before we can understand these other phenomena of the Solid State. It is within a region of dimensions covering groups like these that we look for explanations of many matters which affect our ordinary life—the qualities of a steel or a bronze, of a glass or an insulating compound, of a textile fibre or a nerve. And somewhere in this scale of sizes there enters the breath of life to control those atomic compositions which enter into the living organism. We may never learn any more of the life principle than some details of the mechanism which it employs, but it is fascinating to anticipate that it may be possible to know even that little. What then is this condition of a body which so affects its properties and is superimposed upon the geometric crystalline structure? A survey of all properties and behaviours must be made in the attempt to satisfy such an enquiry. For the purpose of this introductory address I need only allude to one such property: the whole field is in other parts well covered by the excellent reports that have been contributed. The cohesive force in rocksalt calculated from a knowledge of its structure and its ionic composition is about 200 kg. per mm<sup>2</sup>. The experimental value varies greatly with the circumstances of measurement but does not usually amount to a single kilogramme. Plastic working of the specimen generally increases the tensile strength in all materials: so does, in the case of rocksalt, handling under water. What is the cause of this immense discrepancy?

This is one striking example of the effect of the unknown factor: we should perhaps say "factors" to cover the possibility that the causes we are looking for are of a complex character.

Other unexplained discrepancies are described and tabulated in the very interesting paper presented by Dr E. Schmid. He shows how in ionic crystals the calculated elasticity constants agree with observations whereas in the case of the metals there is no agreement at all. So also in considerations of slip, plasticity and mechanical twinning there are great divergences to be explained.

A very important question now presents itself: Is this unknown factor or condition directly due to the characteristic properties of the atoms of which the body is composed? Or is it purely the consequence of external and variable influences? Or does the truth lie between these extremes?

Dr Zwicky would answer the question in the first of these three ways. He has sought to prove the existence of a secondary structure within the crystal on a much larger scale than that revealed by X-rays and so regular that it might also be called crystalline. He has tried to show that beside the regular arrangement of positive and negative ions in an ideal crystal there may be other stable arrangements in which the superstructure plays a part. He has also supposed that in their new positions the ions find themselves in electrical fields and are thereby polarised, so adding to the departure from simplicity which the existence of a superstructure requires. These hypotheses have been strongly criticised, notably by Dr Orowan who is contributing a report to this conference. We shall listen to him with great interest. It is a matter of much regret that Dr Zwicky is not here also: but we are to have the pleasure of hearing our President, when he presents an account of experiments due to Dr Goetz, who has been associated with Dr Zwicky in his researches.

In opposition to Dr Zwicky's idea of the regular superstructure naturally associated with each X-ray structure, are those theories which would suppose the unknown condition to be based on the statistical distribution through the material of some sort of irregularities; gaps, flaws, faults, cracks, "Lockerstellen" are some of the descriptive terms. We are fortunate in having here Dr Orowan, Prof. G. I. Taylor and others who have, with great perseverance and brilliant technique developed the theory originated by Griffith that the unexpected weakness of materials is due to cracks, which are particularly liable to lead to rupture if they lie upon the surface. It is a disappointment that Prof. Joffé, who has done so much to clarify our ideas of the strength of materials, is not

here as he had intended, but we welcome some of his distinguished collaborators who will give an account of the work in Leningrad. We are also very glad to have an account by Dr Burgers of those researches in which he connects the history of the treatment of a crystal with its recrystallization properties: since the latter must also be governed by the condition which we are trying to understand, and a knowledge of any of its effects is therefore valuable.

On the "accidental" hypothesis the condition determining the peculiar behaviour of solid materials is an irregular distribution of defects which is largely determined by outside influences such as rates of cooling from the melt or formation from solution or cold working, or annealing or the nature of the surrounding medium and so on.

It may appear to some that it is possible to push the "accidental" hypothesis too far. It may seem that the remarkable properties of solid materials which mean so much to us cannot be entirely dependent upon external circumstances: that they must be to some extent connected with the characteristic properties of the different atoms. Otherwise it might be possible to expect a similarity in the behaviour of various materials which would far exceed that which is actually observed, considerable as it is. An excuse for the manifold variety of Nature would be lost.

As matters stand therefore we are aware that there is some highly important condition affecting the properties of the solid over and above the regular arrangement revealed by X-ray analysis. This condition has been the subject of much intensive research: which has tried in the first place to distinguish those properties which are sensitive to this unknown condition from those that are not: which has attempted to determine the nature of the condition, weighing the chances of its being accidental against the possibility of its dependence on atomic properties: which has therefore examined on the one hand with much success the consequences of its consisting in the presence of flaws in the crystalline structure and on the other hand has sought to find direct evidence of a crystalline superstructure by calculation and experimental investigation. There is as yet no general agreement. In some directions definite progress has been made, yet it may be that we are only at the beginning of the search for a solution. We are fortunate in that we can now listen to those who have done so much to obtain the material for that solution, and to draw the proper deductions from what has been observed.

A second most important research on phenomena of the Solid State is discussed in the papers of Dr Hückel and Dr Hund who also are here



fortunately to speak of their work. This is a more mathematical investigation. As the details of atomic and molecular structure become clearer, more opportunity is provided for the application of mathematical analysis, particularly in its most recent and most powerful forms. Hückel and Hund have taken a prominent part in this development, and their papers are a valuable summary of the progress that has been made. I cannot attempt in this case any preliminary account of this progress, but must leave our visitors to speak for themselves.

The measured dimensions of crystalline structure must serve, if not always as a starting point, at least as a check upon the results of mathematical analysis. They are more useful, the more accurate they are. It is surely very remarkable that in the case of the co-ordinate binding of organic compounds, the centre-to-centre distances of the atoms should be so invariable. A short table by Dr J. M. Robertson gives the results of some of the most accurate measurements that we have, their accuracy depending on the application of Fourier analysis to careful measurements of the absolute intensities of crystal reflection.

I hope that I have done justice in this short introduction to the great importance and interest of those phenomena of the Solid State which are under discussion at this Conference, and I will not longer stand in the way of those who will describe the researches which they have themselves conducted, and will explain to us their significance.

THE STRUCTURE OF MOLECULES AND OF  
THE IDEAL LATTICE



# AROMATIC AND UNSATURATED MOLECULES

## CONTRIBUTIONS TO THE PROBLEM OF THEIR CONSTITUTION AND PROPERTIES

By ERICH HÜCKEL  
Stuttgart

*ABSTRACT.* The problems dealt with in this paper arose out of the attempt by the author, some years ago, to give a quantum-theoretical basis to the hypothesis that valency forces in a molecule have a definite direction, and to give a quantum-theoretical interpretation of the binding conditions peculiar to aromatic compounds.

In these cases, the classical theory of valency fails, as is shown for example by the insufficiency of the Kekulé scheme. Again, the peculiar behaviour of the substituted benzenes in chemical reactions shows that the influence of a substituted group extends through the whole of the molecule.

A quantum-mechanical treatment would first calculate the "motion" of the electrons, assuming the nuclei fixed, and then find the equilibrium positions of the latter in the combined field of force. It is, as a rule, both unnecessary and impracticable to carry out the full calculations for aromatic and unsaturated compounds. Indeed, it usually suffices to investigate the motion only of the  $\pi$ -electrons (which have anti-symmetrical eigenfunctions with respect to the plane of the molecule) in the framework of the nuclei and the single bond ( $\sigma$ -) electrons.

The coupling between the  $\pi$ -electrons can be calculated by either of two methods. Method I is essentially the well-known one of Heitler and London. Thus this method approximates to the molecular eigenfunctions solely through a given eigenfunction of the separated atoms.

Reasons are given why method I is not applicable to problems of the nature of those studied in this paper. In particular, it is shown that results calculated by Pauling and his collaborators for the energy contents of the different compounds are in disagreement with experiment.

Method II goes back to Lennard-Jones, Hund and Mulliken. It assigns to each electron in a self-consistent field an eigenfunction which extends throughout the whole molecule. This eigenfunction represents modulated waves. In this method it is found for example that all the bonds in the benzene molecule are equivalent, the conception of single and double bonds having lost its meaning. The characteristic parameter in this method is the resonance integral  $\beta$ . The latter is not independently calculated, but its value deduced from the energy contents of a number of different compounds.

The energy contents of a number of aromatic and unsaturated compounds calculated in this way show on the whole good agreement with experiment.

The problem of free radicals (certain groups with "trivalent" carbon atoms, which can exist in solution) is next discussed. It is evident that the energy of dissociation of the dimer of such a radicle must be less than that due to the breakage of a normal C—C linkage. Nevertheless, it is suggested that the bond does not differ materially in structure from an ordinary one. The small energy of dissociation is due to a gain in resonance energy in the aromatic and unsaturated substituents on dissociation.

The same cause which explains the smallness of the work of dissociation of two aromatic-substituted carbon atoms, also accounts for the smallness of the heat of transformation of diamond into graphite.

In the final section, the peculiar position of the rings containing six  $\pi$ -electrons is considered. Some connexions between constitution and chemical properties are discussed.

## SUMMARY OF CONTENTS

§ 1. Introduction . . . . .	10
§ 2. General questions relating to the quantum theory of aromatic and unsaturated compounds . . . . .	11
§ 3. Method I . . . . .	13
§ 4. Method II . . . . .	20
§ 5. Results and discussion of method II . . . . .	23
(a) Energy contents . . . . .	23
(b) Free radicals . . . . .	28
(c) Discussion of chemical properties in relation to constitution . . . . .	33
§ 6. Conclusion . . . . .	35

## § 1. INTRODUCTION

THE problem through which I was led some years ago to a theoretical treatment of the compounds referred to in the title was one of more general significance. It was concerned with the question of whether the dominating hypothesis of organic chemistry—that the forces of valency are directed—could be given a meaning in quantum theory. It appeared at first as if the quantum theory of valency as developed at that time, particularly by Heitler and London\*, left no room for such directivity, and this problem was receiving little attention from physicists. I therefore searched for a quantum theoretical foundation in a simple case in which there is no doubt about this directivity. The example concerned the stability of cis- and trans-substituted ethylene against rotation round the C=C double bond†. This cannot arise from forces of a classical nature between the substituted groups but must depend on features of the structure of the double bond, amenable to treatment only by quantum theory. By utilizing a method developed by Lennard-Jones‡ for diatomic molecules, and, in particular, his treatment of the oxygen molecule O<sub>2</sub>, an explanation of this stability was arrived at§. In ethylene, the pair of electrons which corresponds to the second valency bond has a positional eigenfunction whose nodal plane coincides with that of the molecule, and which is symmetrical in relation to the two carbon atoms ( $\pi$ -linkage of Hund||). The corresponding charge

\* W. Heitler and F. London, *Z. f. Phys.* **44**, 455 (1927). F. London, *ibid.* **46**, 455 (1928); **50**, 24 (1928).

† E. Hückel, *Z. f. Phys.* **60**, 423 (1930).

‡ J. E. Lennard-Jones, *Trans. Far. Soc.* **25**, 668 (1929).

§ The electronic structure of ethylene has been recently treated by essentially the same method by R. Mulliken (*Phys. Rev.* **41**, 751 (1932); **43**, 279 (1933)). Also, by another method, by L. Pauling (*Journ. Amer. Chem. Soc.* **53**, 1367 (1931)). See further G. Penney, *Proc. Roy. Soc. A*, **144**, 333 (1934); *Proc. Phys. Soc.* **46**, 333 (1934).

|| F. Hund, *Z. f. Phys.* **73**, 1 (1931); **73**, 565 (1932).

distribution stabilizes the plane arrangement of the atoms. On the other hand the eigenfunction of the remaining electron-pair concerned in the double bond is nearly axially symmetrical about the C=C-axis and has no stabilizing effect ( $\sigma$ -linkage of Hund\*).

Another problem through which I was led to a further research on the linkages referred to, was that of the special "aromatic" properties of benzene and related compounds†. This appeared to be connected with the failure of the classical system of valency in these cases, evidenced by the insufficiency of the Kekulé scheme and the many, all more or less unsatisfactory, attempts to establish other valency schemes for the aromatic compounds. Further, there was the peculiar behaviour of the substituted benzenes in chemical reactions‡. This behaviour proves that the influence of a substituted group extends through the whole of the molecule, and indeed in a unique manner which is unknown in the saturated compounds. ("Induced alternating polarities§.")

In the course of these investigations the electronic structures of a number of aromatic and unsaturated substances were treated||. In particular an explanation could be given of the stability of aromatically and unsaturatedly substituted radicles¶. Further, it was found possible to bring some of the chemical properties into line with the electronic structures.

## §2. GENERAL QUESTIONS RELATING TO THE QUANTUM THEORY OF AROMATIC AND UNSATURATED COMPOUNDS

The quantum-theoretical treatment of molecular structure makes use of the fact that the velocity of motion of the nuclei is small compared with that of the electrons\*\*. One thus proceeds by investigating the electronic structure in terms of the positions of the nuclei, the motion of the nuclei being then treated as taking place in a potential field arising from the system of electrons and nuclei. In the case of polyatomic molecules it is in practice impossible to carry through this treatment in complete generality. However, it is usually sufficient to investigate the electronic structure for such equilibrium configurations of the nuclei as are known to be stable from chemical experience or through the use of physical methods (interference of Röntgen rays or electrons, and spectra). The treatment may be considerably simplified if the arrangement of the nuclei has some symmetrical features.

For the rest, as regards the unsaturated and aromatic compounds, it is quite unnecessary to carry out a complete treatment of the electronic structure, if information is only desired on special features of these compounds. As a rule, though not

\* F. Hund, *Z. f. Phys.* 73, 1 (1931); 73, 565 (1932).

† E. Hückel, *Z. f. Phys.* 70, 204 (1931).

‡ Chiefly known from the investigations of A. F. Hollemann, *Rec. Trav. Chim.* 1899-1909.

§ D. Vorländer, particularly *Ber. Dt. Chem. Ges.* 52, 263 (1919); 58, 1893 (1925). A. Lapworth, *J. Chem. Soc. London*, 121, 416 (1922). W. O. Kermak and R. Robinson, *ibid.* 121, 427 (1922). E. Hückel, *Z. f. Phys.* 72, 310 (1931).

|| E. Hückel, *Z. f. Phys.* 72, 310 (1931); 76, 628 (1932).

¶ E. Hückel, *Z. f. Phys.* 83, 632 (1933).

\*\* M. Born and R. Oppenheimer, *Ann. d. Phys.* 84, 457 (1927).

in every case\*, it is possible to consider separately those electrons which correspond to one of the two valency bonds comprising a double bond. This results from the following considerations: in the first place it is indicated by chemical experience, and on theoretical grounds it is plausible†, that these electrons are considerably more loosely bound than are those which are to be assigned to single bonds and to the first bond of a double bond ( $\sigma$ -electrons). In the second place, to these electrons are assigned eigenfunctions which, in the case of the plane arrangement usual for unsaturated and aromatic linkages, have a symmetry different from that of the  $\sigma$ -electrons. The latter are in fact symmetrical, and the former anti-symmetrical in relation to the plane of the nuclei. We call the electrons with anti-symmetrical eigenfunctions,  $\pi$ -electrons. The first consideration indicates that a variation in the configuration of the  $\pi$ -electrons as a result of Coulomb forces and polarization, will have small effect on that of the  $\sigma$ -electrons; and the second shows that the resonance action between the two classes of electrons vanishes‡. It is therefore usually sufficient to deal exclusively with the  $\pi$ -electrons—only such cases have so far been dealt with. We thus investigate the distribution of these electrons in the “framework” of the molecule, which may be considered as consisting of the nuclei and a fixed distribution of charge due to the  $\sigma$ -electrons.

According to chemical evidence the molecule of benzene is plane and has a six-fold symmetry. This is at least not in conflict with the results of X-ray and electron-ray analysis§. On this account we consider the  $\pi$ -electrons as being in a framework with this kind of symmetry. Each carbon atom provides three electrons in the  $L$ -level for the three single valency bonds which radiate from it, so that, together with the electrons in the hydrogen atoms, an electron-pair can be assigned to each single bond. We shall not discuss fully here the way in which this arrangement is to be described according to wave mechanics. The essential points are that these electrons form a complete system in the sense of Pauli's principle, and that they have eigenfunctions which are symmetrical with respect to the plane of the ring. Each carbon atom still has one remaining  $L$ -electron, whose eigenfunction has a node in the plane of the ring, and which we name a  $\pi$ -electron. Figure 1 shows qualitatively the charge distribution which is associated with such a  $\pi$ -electron (arbitrary units).

We have now to consider the coupling between these  $\pi$ -electrons. I have already carried out this investigation in my first paper concerning the benzene molecule, using two methods||:

\* As an example of a system of atoms in which this is not the case we may consider the radicle  $(C_6H_5)_2C-C(C_6H_5)_2$ , in which, for the accepted space arrangement of the atoms, a resonance action is possible, for reasons of symmetry, between the  $\sigma$ -electrons in the tetravalent carbon atom and the  $\pi$ -electrons of the remaining carbon atoms. This is probably connected with the marked stability of this radicle.

† F. Hund, *Z. f. Phys.* 73, 1, 457 (1931); 73, 565 (1931).

‡ Cf. note \*, above.

§ In the interpretation of the Raman spectrum of benzene, however, the acceptance of this kind of symmetry leads to difficulties. (G. Placzek, *Leipziger Vorträge*, Hirzel, 1931, p. 100.) Since there is no evidence for any other definite structure, we thus adhere to the plane arrangement and six-fold symmetry.

|| Both methods were previously employed by Bloch for the treatment of the forces between electrons in crystal lattices. F. Bloch, *Z. f. Phys.* 52, 555 (1928); 61, 206 (1930).

- I. The method of Heitler and London (Method I).
- II. The method of Lennard-Jones, Hund and Mulliken (Method II).

## §3. METHOD I

The first method was carried through following a mathematical treatment of Slater\*. Pauling† has since used an essentially simpler mathematical procedure, which goes back to Weyl and Rumer‡, for calculating the states of least resultant total spin  $s$  (in this case  $s = 0$ ) to which the fundamental state always belongs. This

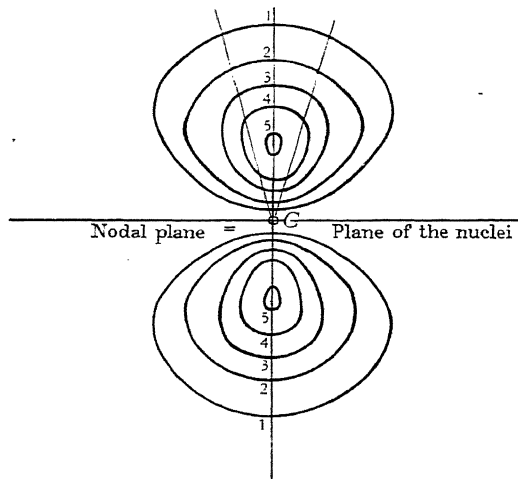


Figure 1. Curves of constant charge density in a plane through a C-nucleus, perpendicular to the plane of the nuclei.

method, however, differs from the earlier one only in the mathematical treatment, and thus leads to the same results. Method I commences, as regards the coupling referred to above, by assigning to each carbon atom a  $\pi$ -electron which is in a given state with the positional eigenfunction  $\phi_a(r_{ia})$  (the suffixes indicating the  $i$ th electron in the atom  $a$ ). The total positional eigenfunction, taking coupling into account, is written as a linear combination of the products  $\phi_1(r_{i1}) \dots \phi_6(r_{i6})$ , and, starting from this, the Heitler-London perturbation method is worked out (to the first approximation). Of course, only such linear combinations are considered as satisfy the Pauli principle when the spin is allowed for. (Coupling between spin and orbit, as well as between the spins themselves, is neglected.) The Rumer-Pauling method now proceeds by selecting from these linear combinations those which correspond to the smallest value of the total spin (in this case  $s = 0$ ), and choosing from these, in a certain way, the ones which are linearly independent. These functions which belong to the value  $s = 0$ , can be associated with models

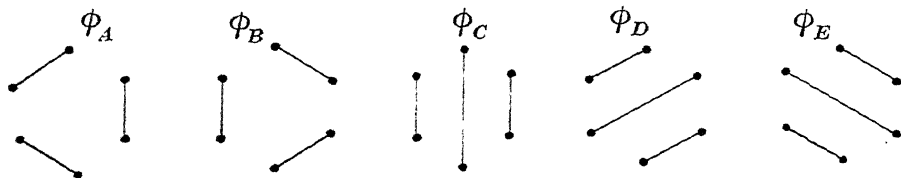
\* F. C. Slater, *Phys. Rev.* **34**, 1293 (1929); **35**, 511 (1930).

† L. Pauling, *J. Chem. Phys.* **1**, 280 (1933). L. Pauling and G. W. Wheland, *ibid.* **1**, 362 (1933).

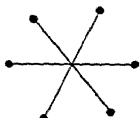
‡ H. Weyl, *Nachr. der Ges. der Wiss., M.-Ph. Klasse*, p. 285 (1930); p. 33 (1931). G. Rumer, *ibid.* p. 337 (1932). G. Rumer, E. Teller and H. Weyl, *ibid.* p. 499 (1932).



of the valency pattern (of the  $\pi$ -electrons) in which the atoms are joined in pairs by single bonds, one and only one bond radiating from each atom in such a way that the bonds do not cross one another\*. The schemes of valencies corresponding to the functions so chosen are called by Pauling "canonical structures." The problem of secular perturbations corresponding to these functions may be formulated and solved by a method due to Rumer and Pauling for the case where attention is confined to coupling between adjacent atoms. In the case of benzene there are five canonical structures with corresponding "canonical functions":



$A$  and  $B$  correspond to the Kekulé forms,  $C$ ,  $D$  and  $E$  to the Dewar forms. To every other structure, for example that of Claus:



there is a corresponding linear combination of the canonical functions,

$$\phi_{\text{Claus}} = \phi_A + \phi_B - [\phi_C + \phi_D + \phi_E].$$

The canonical functions are not "eigenfunctions"; in other words, they do not represent states of definite energy. In fact, to the states of definite energy there correspond linear combinations of the canonical functions which, with the corresponding eigenvalues, are determined from the perturbation problem. Denoting by  $J_0$  the Coulomb integral and by  $J$  ( $J < 0$ ) the exchange integral of the theory of Heitler and London, each for the  $\pi$ -electrons of two adjacent atoms, then the solution of the perturbation problem gives for the coupling energy and the eigenfunction of the  $\pi$ -electrons in the ground state of benzene the expressions

$$6J_0 + (\sqrt{13} - 1)J = 6J_0 + 2.6055J;$$

and

$$\phi = 0.62435 (\phi_A + \phi_B) + 0.27101 (\phi_C + \phi_D + \phi_E).$$

Thus, in the sense of the method of approximation employed, the ground state may be considered as resulting from the superposition of the two Kekulé and the three Dewar forms. The ground state possesses six-fold symmetry, in agreement with chemical evidence.

For illustration, the total coupling energy of the ground state may be split up. For a Kekulé system by itself the "exchange energy" (e.e.) would have the value  $\frac{3}{2}J$  and for a Dewar system the value 0. The difference between the actual e.e. and that for a Kekulé system alone ( $1.1055J$ ) may be referred to as the "resonance energy"

\* In general crossing cannot take place if the atoms—independently of their actual configuration in space—are regarded as being arranged on a circle.

(r.e.) of the structure (taken in relation to a Kekulé system). This again may be regarded as split up into a reciprocal r.e. of the two Kekulé structures and a remainder (the first fraction has the value 0.9  $J$  and the second 0.2055  $J$ ).

Pauling and his co-workers\* have applied method I to a whole series of aromatic and unsaturated compounds, and, among other applications, have employed it for treating free radicles with aromatic substituents for whose stability they gave an explanation. They have further discussed the connexion between the results and the energy content of the substances. In contrast to this I considered as early as my first work on benzene, that I had been able to show that method I was unsuitable for handling the coupling of the  $\pi$ -electrons, since it appeared that this method leads to results which are not in agreement with experiment.

Method I confines itself to the first approximation of the Heitler-London theory. Thus in the first place the objections which may be brought against the application of the method from a purely theoretical standpoint, are the same as may be raised generally against the applicability of this approximation. The method approximates to the eigenfunctions in the molecule solely through a given eigenfunction of the separate atoms, while in reality, the eigenfunctions of the higher states of the separate atoms are more or less involved in the molecular functions. This may also be expressed as a neglect of the capacity for polarization which must be taken into account in the next approximation of the Heitler-London theory. Also, no attention is given to the possibility that in a single atom there may be two electrons in the same state ("polar states" of Slater). It is very difficult to estimate in a given case to what extent the quantitative results will be affected by the neglect of these considerations. On the other hand the principal advantage of method I is that its formal scheme goes far to provide a picture of the arrangement of the valencies and shows how the classical scheme of valencies, which fails here, may be extended so that a state may be considered as arising from the superposition of different valency patterns. However, this advantage is naturally not sufficient if the quantitative results cannot be brought into agreement with experience, whereas as we shall see this will be the case for the results of method II. The failure of method I is shown by the following considerations:

(1) Method I leads to results for the energy content of aromatic and unsaturated compounds which are not in agreement with experiment. (This is established here for the first time.)

(2) It fails to indicate the distinctive nature of rings with six  $\pi$ -electrons.

(3) For substituted benzenes, there follows from it a disturbance of the charge distribution in the molecule, resulting from the substitutions which cannot be brought into correspondence with the reactive properties of the substituted benzene.

We shall consider below the evidence on which these assertions are based.

*Concerning* 1. Method I always gives a smaller absolute value for the e.e. per  $\pi$ -electron in conjugated and aromatic systems, i.e. a smaller binding energy (larger

\* L. Pauling and G. W. Wheland, *J. Chem. Phys.* 1, 362 (1933). L. Pauling and J. Sherman, *ibid.* 1, 606 (1933); 1, 679 (1933). [Note added in proof: See also G. W. Wheland, *ibid.* 2, 474 (1934); J. Sherman, *ibid.* 2, 488 (1934).]

energy content), than in an isolated double bond. In contradistinction to this it is known that the binding energy is always greater (i.e. the energy content is smaller) for conjugated and aromatic systems than the value which would be calculated from the isolated double bonds. For example, the e.e. of benzene according to method I is  $2.6055J$ , and the e.e. for three isolated double bonds amounts to  $3J$ . Thus according to this benzene would have a smaller binding energy than would be associated with three isolated double bonds. The observed binding energy is, however, greater. Pauling and Sherman give the energy content (negative binding energy) as  $E = -58.20$  e.V. (observed) and  $E' = -56.58$  e.V. (estimated for three separate double bonds)\*. Nevertheless these authors come to the conclusion that the result of method I is in agreement with experiment. This claim, however, is based on an erroneous method of calculation. The authors in fact set the difference  $E - E'$  equal to the resonance energy referred to a Kekulé structure:

$$E - E' = -1.62 \text{ e.V.} = 1.1055J,$$

and so obtain  $J = -1.5$  e.V. It is not, however, permissible to set these two quantities equal to one another. For  $E'$  is calculated with the binding constant of an isolated double bond;  $E' = 3 \cdot (C-C) + 3 \cdot (C=C) + 6 \cdot (C-H)$ , and three isolated double bonds have the value  $3J$  for the e.e. In contradistinction to this the Kekulé structure, to which the r.e. refers, has an e.e. equal only to  $\frac{3}{2}J$ .

Denoting by  $E'$  and  $E$  the calculated and observed energy contents (negative binding energies) respectively we may write

$$\begin{aligned} E' &= E_0 + 3J, \\ E &= E_0 + \frac{3}{2}J + 1.1055J, \end{aligned}$$

where  $E_0$  has the same value in both equations and denotes the energy content apart from the exchange energy, since, of course,  $E'$  and  $E$  should only differ from each other as a result of the different value of the e.e. for three isolated double bonds and for the benzene structure respectively. (Pauling and Sherman's argument implies the incorrect statement  $E' = E_0 + \frac{3}{2}J$ .) Then follows

$$E - E' = -1.62 \text{ e.V.} = (1.1055 - \frac{3}{2})J,$$

so that  $J > 0$  (repulsion instead of attraction!) and *not* as according to Pauling and Sherman

$$E - E' = -1.62 \text{ e.V.} = 1.1055J.$$

In a similar way all the calculations of Pauling and Sherman are in error†, wherever the differences between the values  $E'$  calculated from the binding constants and the actual values  $E$  have been identified with the resonance energies deduced from quantum theory.

The results of method I are therefore not in agreement with experiment as regards

\* These binding energies, unlike those usually adopted, are referred to a separation into C-atoms which are in a state 1 e.V. higher than the normal, instead of to the latter condition itself. (It was at that time assumed that separation resulted in C-atoms in the  $^4S$  state, and that this lay 1 e.V. above the ground state. Although we now know that the latter is not true, we can use the values given above, since only their differences occur here, and these are independent of which state of the free C-atom is used as standard for the binding energies.) 1 e.V. = 23.054 k. cal./mol.

† Note added in proof: The same holds for the recent work of G. W. Wheland, *J. Chem. Phys.* 2, 474 (1934).

the energy content. But it is worthy of note that for various compounds the *differences* between the resonance energies calculated by Pauling and Sherman for the different compounds in general coincide quite well with the *differences* in the values of  $E - E'$  calculated by their method.

*Concerning 2.* Method I is unable to explain why rings containing six  $\pi$ -electrons possess a remarkably stable configuration of electrons; nor why although the five-ring enters as an ion into such combinations as  $[C_5H_5]^-K^+$ , yet no compounds such as  $[C_7H_7]^-K^+$  are known. Further, why hetero-cyclic rings with five atoms, such as pyrrole  $(CH)_4NH$ , to which six  $\pi$ -electrons must be attributed, are fairly similar in their chemical properties to the aromatic compounds. That the symmetrical arrangement of the valencies at angles of  $120^\circ$  cannot be entirely responsible for this, but rather that it depends on the number, six, of the  $\pi$ -electrons, is shown most clearly by the existence of metallic compounds of  $[C_5H_5]^-$  and the non-existence of such compounds of  $[C_7H_7]^-*$ . For the five-ring itself,  $C_5H_5$ , method I leads to a very small e.e.:  $1.23607J$ . The seven-ring has not been calculated. The ions are not amenable to treatment by this method.

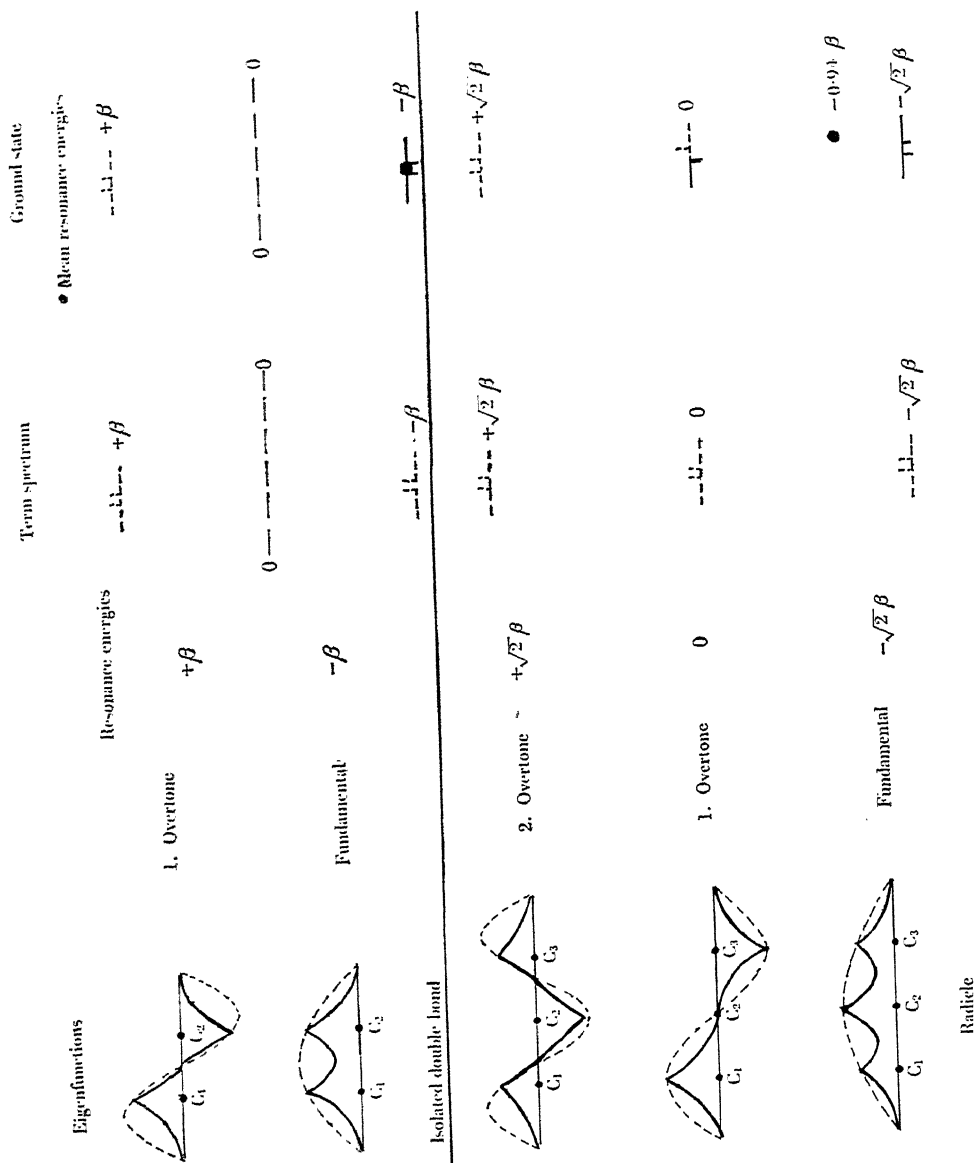
*Concerning 3.* In the case of reactions with substituted benzenes (for example, the nitration of toluene) it is known that the different possible reaction products (*o*-, *m*-, *p*-nitrotoluene,  $C_6H_4CH_3NO_2$ ) are not produced to the same extent (a "directive action" of the substituent). The differences of the heats of activation  $Q$  for the example mentioned are, in k. cal./mol.:

$$Q_o - Q_p = 135, \quad Q_m - Q_o = 1490, \quad Q_m - Q_p = 1625,$$

while the activity constants  $A$  are approximately equal†. The principal products are then the *o*- and *p*-, and only to a small extent the *m*-compound. If instead of the "negative" substituent  $CH_3$  we have a "positive" one, for example  $COOH$ , the relations are reversed. In the nitration of benzoic acid, for instance,  $Q_m - Q_o = -800$  and  $Q_p$  is so large that the *p*-compound is usually not produced in a measurable quantity. This shows that the different heats of activation are determined by the character of the substituted group, the influence of which extends through the whole molecule ("induced polarities"). Since this kind of action is not known in the case of unsaturated compounds, the different heats of activation for the *o*-, *m*- and *p*-compounds must be determined by the disturbance of the configuration of the  $\pi$ -electrons by the substituent. The relative magnitudes of the alterations in the charge density of these electrons in the *o*-, *m*- and *p*-atoms can be calculated from the electronic structure of the ground state and the excited states of the  $\pi$ -electrons. In this way from the states determined by method I, we obtain modifications of the charge distribution which are equal in the *o*- and *m*- and less in the *p*-form. According to method II, on the other hand, we obtain ratios for these disturbances which are in step with the heats of activation of the different forms. The reason is,

\* As regards the significance of the number 6 of "double bond ( $\pi$ ) electrons" in the 5-rings, see the discussion by W. Hückel, *Theoretische Grundlagen der organischen Chemie*, 2nd edition, 1, 386 et seq. (1934).

†  $A$  and  $Q$  are defined by the formula of Arrhenius  $K = Ae^{-Q/RT}$  for the constant  $K$  of the reaction velocity.



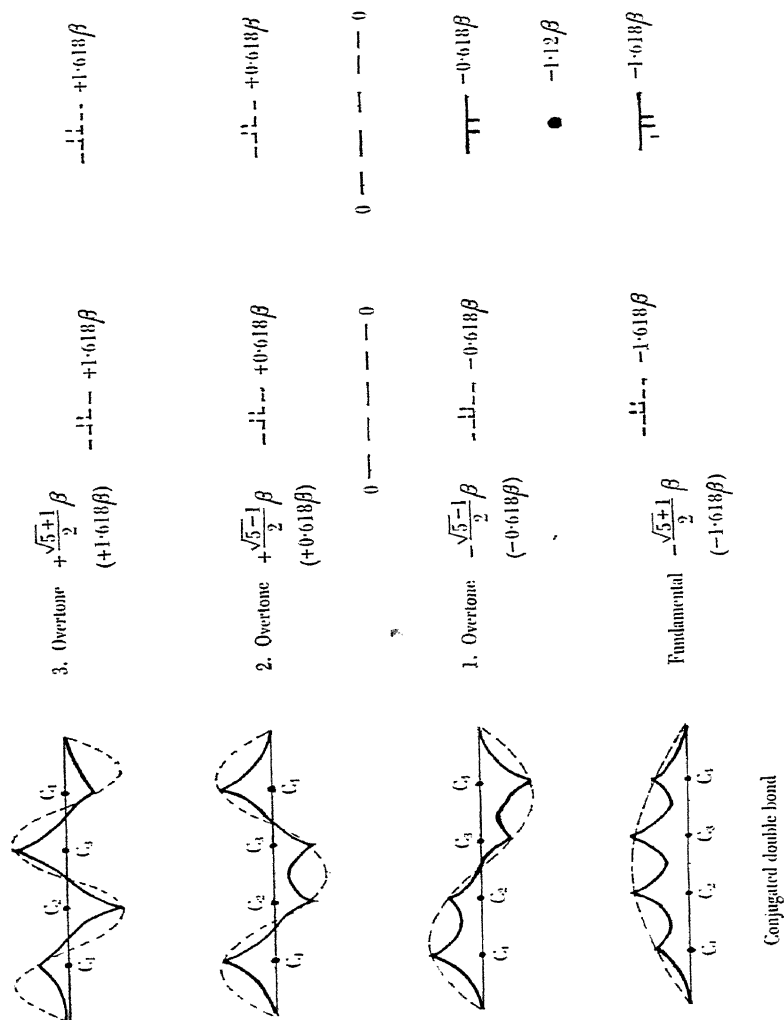


Figure 2

that in method I only some of the excited states are obtained, while the polar states of Slater are not considered.

#### § 4. METHOD II

In method II (which Mulliken calls the method of "molecular orbitals") to each electron is assigned an eigenfunction which extends through the whole of the molecule. These, and the associated eigenvalues are to be conceived as in a "self-consistent" (Hartree) field which arises from the charge of the nuclei and the statistical charge distribution of all the electrons apart from the one directly under consideration. In this case also, the  $\pi$ -electrons may be considered separately, since in the different compounds, the charge distribution of the other electrons in a carbon atom and the distances of separation of the nuclei are treated as independent of the coupling of the  $\pi$ -electrons to the first approximation. The method proceeds by first taking the Hartree field as being independent of the state in which a single electron is considered to be. This Hartree field may be represented as a superposition of the Hartree fields  $V_f$  associated with the individual atoms

$$V(r) = \sum_f V_f(r - R_f) \quad \text{.....(1)}$$

( $f$  is a number identifying the particular atom,  $r$  the position vector of an electron and  $R_f$  that of the  $f$ th C-nucleus).

At the same time  $V_f$  is taken to have the same value for all the atoms\*.

Denoting then by  $\psi_f^{(0)}$  the eigenfunction corresponding to the lowest eigenvalue  $W^{(0)}$  of a  $\pi$ -electron in the field  $V_f$ , the eigenvalues and eigenfunctions in the field  $V$  are written as

$$W^{(k)} = W^{(0)} + \Delta W^{(k)} \quad \chi^{(k)} = \sum_f a_f^{(k)} \psi_f^{(0)}(r - R_f) \quad \text{.....(2)}.$$

The  $\Delta W^{(k)}$  and the corresponding set of coefficients  $a_f^{(k)}$  are then determined from a problem of secular perturbations. If the coupling between adjacent atoms only is considered, and if the non-orthogonality of the eigenfunctions of adjacent atoms is neglected,  $\Delta W^{(k)}$  always has the form

$$\Delta W^{(k)} = -\alpha + b\beta \quad \text{.....(3)}.$$

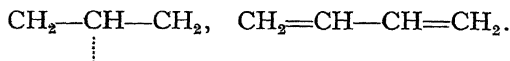
Here  $\alpha$  is the "Coulomb integral"

$$\alpha = -\frac{1}{2} \int (\psi_1^{(0)*} V_1 + \psi_2^{(0)*} V_2) d\tau > 0 \quad \text{.....(3a)},$$

and  $\beta$  is the "resonance integral"

$$\beta = -\frac{1}{2} \int \psi_1^{(0)} \psi_2^{(0)} (V_1 + V_2) d\tau > 0 \quad \text{.....(3b)}$$

(1 and 2 being adjacent atoms);  $b$  is a numerical factor. The functions  $\chi^{(k)}$  represent modulated waves. The course of these functions along the chain of carbon atoms is shown qualitatively in figure 2, for the isolated double bond and the systems as involved in



\* The values of  $V_f$  could also, of course, be considered as being different: for example we should strictly distinguish between  $V_f$  for such carbon atoms as have three other carbon atoms adjacent to them, and for those having two or only one (as, for example, in naphthalene or at the ends of a chain).

(The functions have opposite values above and below the plane of the molecule.) We always obtain as many states as there are C-atoms present. States in which  $b < 0$  are binding, while those with  $b > 0$  are loosening owing to the resonance. The ground state is arrived at by filling up the  $\chi^{(k)}$ 's in order of increasing energy, so that each state is not occupied more than twice. The total energy of coupling is equal, in the sense of Hartree's method, to the sum of the coupling energies for the occupied  $\chi^{(k)}$  states.

In this connexion, states with negative values of  $b$  contribute to binding and states with positive values of  $b$  to a loosening of the atoms. A state which has no nodes between two atoms leads to an attraction while one which has a node there leads to a repulsion between the two atoms. In conjugated systems the bonds cannot be localized or can only be partially localized. So for example in the ground state of butadiene two of the occupied states link all four carbon atoms. The two other states link the outermost atoms  $C_1, C_2$  and  $C_3, C_4$ , but loosen  $C_2, C_3$ . Corresponding to this the central binding is weaker, but is nevertheless not an ordinary single bond. Since the charge density of the  $\pi$ -electrons is relatively small there, this linkage will be less stable against rotation than a double bond. This applies in a corresponding way to the binding between the central carbon atoms in diphenyl. The result is in agreement with chemical evidence, according to which there is no rigidity against rotation between the atoms  $C_2$  and  $C_3$ . Nevertheless we have to admit that for these linkages also the plane arrangement is the most stable. (It may be, however, that a non-plane arrangement is forced to be stable by voluminous substituted groups; compare for instance the *o*- and *o'*-derivatives of diphenyl.) It is especially in benzene that all the bonds are equivalent. The representation with double and single bonds loses its meaning in this case.

In figure 2 the resonance energies are also shown. The Coulomb action is always proportional to the number of carbon atoms. In the figure  $\text{---}\vdots\text{---}$  denotes a state which can be occupied twice (not degenerate),  $\text{---}\text{||}\text{---}$  such a state doubly occupied, and  $\text{---}\dot{\text{---}}$  such a state singly occupied. The point  $\bullet$  indicates the mean resonance energy per  $\pi$ -electron. (Term centre for the occupied states.)

In criticism of method II the following is worthy of note. The method appears at first to neglect the exchange action between the electrons, and in fact the Hartree method as normally used also has this feature. It may be shown, however, that for the ground state, where either all the occupied states are occupied in pairs, or all in pairs except one, the exchange is largely taken into account if by the expression  $V_f(\mathbf{r} - \mathbf{R}_f)$  in (1) we understand the following sum\*:

$$V_f = V_f^0 + \frac{1}{2}v_f \quad \dots\dots(4),$$

\* The method of proof of the theorem used here corresponds to the treatment given by Fock (V. Fock, *Z. f. Phys.* 61, 126 (1930), T. Koopmanns, *Physica*, 1, 104 (1934)). Fock's equations may be written (in Hartree units)

$$\left[ H(\mathbf{r}) + \sum_k \left( \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right)_{kk} - W^{(i)} \right] \chi^{(i)}(q) = \sum_k \chi^{(k)}(q) \cdot \left( \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right)_{ki},$$

where  $q$  denotes  $x, y, z$  and the spin components  $\sigma_i$  in a given direction.  $\left( \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right)_{ki}$  are the matrix



where  $V_f^0$  is the potential which arises from the nucleus and the  $\sigma$ -electrons of the  $f$ th atom;  $v_f$  is the potential arising from the charge distribution  $\psi_f^{(0)}$  itself:

$$v_f = \int \frac{\psi_f^{(0)*}(\mathbf{r}' - \mathbf{R}_f) e^2}{|\mathbf{r} - \mathbf{r}'|} d\tau' \quad \dots\dots(4a);$$

and  $\psi_f^{(0)}$  is the lowest eigenvalue of the eigenfunctions belonging to the Schrödinger equation

$$\frac{8\pi^2 m}{h^2} [W - V_f(\mathbf{r} - \mathbf{R}_f)] \psi_f(\mathbf{r} - \mathbf{R}_f) = 0 \quad \dots\dots(4b).$$

In order that the exchange may be largely allowed for it is always essential that the influence of  $\frac{1}{2}v_f$  on the resonance energy should be small compared with that of  $V_f^{(0)}$ . It is then also permissible to regard the Hartree field  $\sum_f V_f$  as being approximately the same for all the  $\chi^{(k)}$ -states. This hypothesis may be realized. We may also further assume for molecules with a larger number of  $\pi$ -electrons that in cases where only two states are not doubly occupied, the exchange is sufficiently accounted for by (4).

Method II, in contrast to I, takes account of the polar states. It is, however, not correct to say, without further proof, that the method gives far too great consideration to these states. This would only be correct without doubt if the eigenfunctions in the field  $V_f^0$  (and not in  $V_f$ ) were used for the approximation, with simultaneous neglect of the exchange. After all it cannot be stated without further examination how large are the errors which arise from the fact that only linear combinations of functions of the form  $\chi^{(1)}(r_{i1}) \dots \chi^{(n)}(r_{in})^*$  are permitted as solutions of the complete Schrödinger equation.

If we give preference to method II over method I, notwithstanding the uncertainties from the theoretical standpoint as to how far the two methods represent an approximation to the truth, the reason is that it has been shown that method II represents largely the facts of experiment, and particularly in cases where method I has been proved to be inadequate. We grant that this state of affairs is unsatisfactory from a purely theoretical standpoint. Considering, however, the great difficulties which present themselves in a quantitative estimation of the limits of accuracy, it appears scarcely possible to renounce the heuristic point of view.

elements of  $\frac{1}{|\mathbf{r} - \mathbf{r}'|}$  in the system of the  $\chi^{(k)}(q)$ . The summation extends over all the occupied states. Finally, we have  $H(r) = -\frac{\Delta}{2} + \sum_f V_f^{(0)}(\mathbf{r} - \mathbf{R}_f)$ . From this and from the equation

$$\chi^{(i)}(r) = \sum_f a_f^{(i)} \psi_f^{(0)}(\mathbf{r} - \mathbf{R}_f)$$

the result given above follows if the terms which involve the products  $\psi_f^{(0)} \psi_{f+1}^{(0)}$ ;  $\psi_f^{(0)} \psi_{f+2}^{(0)}$  are neglected as being small compared with the terms involving  $\psi_f^{(0)}$ . If neglect of these terms is to be permissible it is essential that the influence of  $\frac{1}{2}v_f$  on the resonance action shall be small compared with that of  $\Delta_f^{(0)}$ .

\* Cf. R. S. Mulliken, *Phys. Rev.* 41, 68 et seq. (1932).

## § 5. RESULTS AND DISCUSSION OF METHOD II

Consequently we confine ourselves below to the results of method II, and to the discussion of the conclusions which can be drawn from these results as regards the constitution and properties of the compounds dealt with here.

(a) *Energy contents*

We obtain, in the first place, information on the relative energy contents of different aromatic and unsaturated compounds, and indeed (unlike that furnished by method I) it is not in qualitative disagreement with experience. Table 1 gives a survey of the resonance energies as multiples of  $\beta$  for a series of compounds. It should be noted that in the calculation, the same  $V_f$  has been ascribed to every C-atom: for example in naphthalene all the C-atoms are considered as equivalent. Since it is difficult to express the deviations for the different C-atoms, we have hitherto not attempted to take account of these differences.

A part of the data of table 1 is set out in figure 3. In this, a black spot ● represents the mean energy of binding per  $\pi$ -electron in the ground state of the molecule. We shall later with the aid of this figure discuss some correlations between electron structure and properties.

The resonance integral  $\beta$  is the characteristic magnitude of the theory. To calculate its value theoretically would be exceedingly difficult. On the other hand, we can derive its value from the observed energy content of different aromatic and unsaturated compounds. Thus from the energy content  $E = -58.20$  e.V., and the value  $E' = -56.58$  e.V. calculated (see p. 16) from the binding constants (for three separate double bonds), we have, from the relations

$$E = E_0 - 8\beta; \quad E' = E_0 - 6\beta,$$


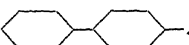
the equation 
$$\beta = \frac{E' - E}{2} = 0.81 \text{ e.V.} = 18.7 \text{ k. cal./mol.}$$

However, the calculation of  $\beta$  by means of the binding constants is not wholly free from doubt, since the binding constants contain a certain arbitrariness. This arbitrariness arises mainly because the binding constants of the C—H bond in aliphatic, unsaturated and aromatic compounds have been assumed the same. Elsewhere, I have shown\* how the value of  $\beta$  can be determined from the heats of hydrogenation in the case of benzenes having different heats of hydrogenation, without using the binding constants. This method of calculation involves only the assumption that the structure of the  $\sigma$ -bond is not changed by the resonance effect of the  $\pi$ -electrons, and that the magnitudes  $\alpha$ ,  $\beta$  can be assumed equal for all C-atoms with a  $\pi$ -electron. It agrees therefore with the assumptions and simplifications (cf. p. 20) underlying the theory. By the method stated, the result found is  $\beta = 15$  k. cal./mol. The uncertainty of this value is due to the inaccuracy with which the heats of hydrogenation are known. On this account, and since the use of the binding constants cannot generally be avoided in this way, exact calculation of the energy contents is not possible. Nevertheless using the binding constants

\* E. Hückel, *Z. f. Phys.* 83, 665 (1933).









Table I

Substance and type	Number of $\pi$ -electrons	Resonance energy in ground state	Mean resonance energy per $\pi$ -electron in ground state	Resonance energy of highest occupied state	Number of electrons in highest occupied state	Number of vacant positions in highest occupied state	Resonance energy of lowest unoccupied state
1. Conjugated systems:							
$\text{H}_2\text{C}=\text{CH}_2$	2	-2 $\beta$	- $\beta$	- $\beta$	2	0	$\beta$
$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$	4	-4.48 $\beta$	-1.12 $\beta$	-0.62 $\beta$	2	0	0.62 $\beta$
$\text{H}_2\text{C}(\text{CH})_2\text{CH}_2$	6	-6.96 $\beta$	-1.16 $\beta$	-0.445 $\beta$	2	0	0.445 $\beta$
$\text{H}_2\text{C}(\text{CH})_3\text{CH}_2$	8	-9.52 $\beta$	-1.19 $\beta$	-0.345 $\beta$	2	0	0.345 $\beta$
$\dots$	$\dots$	$\dots$	$\dots$	$\dots$	$\dots$	$\dots$	$\dots$
$\text{H}_2\text{C}(\text{CH})_\infty\text{CH}_2$	$\infty$	$\infty$	-1.27 $\beta$	0 $\beta$	2	0	0 $\beta$
$\text{H}_2\text{C}(\text{CH})\text{CH}_2$	3	-2.82 $\beta$	-0.94 $\beta$	0 $\beta$	1	1	0 $\beta$
$\text{H}_2\text{C}(\text{CH})_2\text{CH}_2$	5	-5.54 $\beta$	-1.09 $\beta$	0 $\beta$	1	1	0 $\beta$
$\text{H}_2\text{C}(\text{CH})_3\text{CH}_2$	7	-8.05 $\beta$	-1.15 $\beta$	0 $\beta$	1	1	0 $\beta$
$\dots$	$\dots$	$\dots$	$\dots$	$\dots$	$\dots$	$\dots$	$\dots$
$\text{H}_2\text{C}(\text{CH})_\infty\text{CH}_2$	$\infty$	$\infty$	-1.27 $\beta$	0 $\beta$	1	1	0 $\beta$
2. Rings:							
$[\text{C}_4\text{H}_4]$	4	-4 $\beta$	- $\beta$	0 $\beta$	2	2	0 $\beta$
$[\text{C}_6\text{H}_6]$	6	-8 $\beta$	-1.333 $\beta$	-0.62 $\beta$	3	1	0.62 $\beta$
$[\text{C}_8\text{H}_8]$	8	-9.68 $\beta$	-1.21 $\beta$	- $\beta$	4	0	$\beta$
$[\text{C}_{10}\text{H}_{10}]$	10	-13.683 $\beta$	-1.368 $\beta$	-0.618 $\beta$	2	0	0.618 $\beta$
3. Condensed systems:							
Naphthalene $\text{C}_{10}\text{H}_8$	10	-13.683 $\beta$	-1.368 $\beta$	-0.618 $\beta$	2	0	0.618 $\beta$
Anthracene $\text{C}_{14}\text{H}_{10}$	14	-19.314 $\beta$	-1.379 $\beta$	-0.414 $\beta$	2	0	0.414 $\beta$
4. Aromatic unsaturated:							
Diphenyl $\text{C}_{12}\text{H}_{10}$	12	-16.383 $\beta$	-1.365 $\beta$	-0.705 $\beta$	2	0	0.705 $\beta$
$\text{Ph}-\text{C}=\text{C}-\text{Ph}$	14	-18.878 $\beta$	-1.349 $\beta$	-0.504 $\beta$	2	0	0.504 $\beta$
$\text{Ph}-\text{C}(\text{CH}_3)-\text{C}(\text{Ph})_2$	16	-24.401 $\beta$	-1.338 $\beta$	-0.386 $\beta$	2	0	0.386 $\beta$
$\text{Ph}-\text{C}(\text{CH}_3)_2-\text{C}(\text{Ph})_2$	18	-23.934 $\beta$	-1.330 $\beta$	-0.311 $\beta$	2	0	0.311 $\beta$
$(\text{Ph})_2\text{C}=\text{C}(\text{Ph})_2$	26	-35.719 $\beta$	-1.374 $\beta$	-0.368 $\beta$	2	0	0.368 $\beta$
$\text{Ph}(\text{CH})\text{Ph}$	13	-17.301 $\beta$	-1.331 $\beta$	0 $\beta$	1	1	0 $\beta$
$\text{PhC}(\text{CH})\text{CPh}$	15	-19.911 $\beta$	-1.327 $\beta$	0 $\beta$	1	1	0 $\beta$
$(\text{Ph})_2\text{C}(\text{CH})\text{C}(\text{Ph})_2$	27	-36.830 $\beta$	-1.364 $\beta$	0 $\beta$	1	1	0 $\beta$
5. Stable free radicals:							
$\text{C}(\text{Ph})_3$	19	-25.794 $\beta$	-1.357 $\beta$	0 $\beta$	1	1	0 $\beta$
$\text{C}(\text{Ph})_2\text{Diph}$	25	-34.302 $\beta$	-1.368 $\beta$	0 $\beta$	1	1	0 $\beta$
$\text{CPh}(\text{Diph})_2$	31	-42.607 $\beta$	-1.374 $\beta$	0 $\beta$	1	1	0 $\beta$
$\text{C}(\text{Diph})_3$	37	-51.082 $\beta$	-1.381 $\beta$	0 $\beta$	1	1	0 $\beta$
Pentaphenyl cyclopentadienyl $\text{C}_{39}\text{H}_{30}$	35	-48.15 $\beta$	-1.376 $\beta$	-0.33 $\beta$	3	1	-0.33 $\beta$
A cleavage plane of the graphite lattice	$\infty$	$\infty$	-1.58 $\beta$	0 $\beta$	—	—	0 $\beta$

Ph denotes  and Diph denotes .

we find on the whole that the energy contents of aromatic and unsaturated agree fairly well with the theory, using the approximate value  $\beta = 20$ . Table 2 contains a short list of some compounds from which this may be seen. If  $E$  is the observed and  $E'$  the energy content\*, calculated from the binding constants of just so many  $C=C$  bonds as the molecule contains double bonds, then  $E' - E$  is interpreted as the difference between the resonance energy  $-2z\beta$  for  $z$  separate bonds, and the

Table 2. Energy contents

Compounds (formulated with double bonds)	$-E$ , where $E$ is observed energy content k. cal./mol.	$-E'$ , where $E'$ is energy content calculated from binding constants k. cal./mol.	$E' - E$ k. cal. mol.	$x\beta$ theoretical	$x\beta$ for $\beta = 15$ k. cal./mol.	$x\beta$ for $\beta = 20$ k. cal./mol.	$\frac{E' - E}{x} = \beta$ k. cal./mol.
 Benzene		1165	37	$2\beta$	30	40	18.7
 1, 2 dihydrobenzene		1306.5	1298	8.5	$0.48\beta$	6.7	17.7
 1, 2, 3, 4 tetrahydrobenzene		1424.5	1430	5.5	$0\beta$		
 Cyclohexane		1547	1562	15			
 Naphthalene		1904	1828	76	$3.68\beta$	55	20.6
 Anthracene		2595	2490	105	$5.314\beta$	80	19.7
 Diphenyl		2305	2217	88	$4.383\beta$	66	88
 Stilbene		2701	2606	95	$4.878\beta$	73	19.5

The values of the binding constants used (from Pauling and Sherman, calculated for the C-atom in the ground state) are  $(C-H) = 93.9$ ,  $(C-C) = 72.6$  and  $(C=C) = 128.3$ .

true resonance energy. If this is  $> 0$  it means that the resonance effect gives a smaller energy content than has been calculated for the corresponding number of separate double bonds. It is obtained theoretically from the results given in table 1 as a multiple of  $\beta$ , viz.  $x\beta$ .

\* In part these have been taken from the work of Pauling and his collaborators, but they are calculated here for the C-atom in the normal state. (Cf. p. 16, f.n.) Here therefore  $E'$  is as many electron volts less than Pauling's figures as there are C-atoms in the molecule, and the binding constants are less by  $\frac{1}{2}$  for  $C-H$ , by  $\frac{1}{2}$  for  $C-C$  and by 1 e.v. for  $C=C$ .

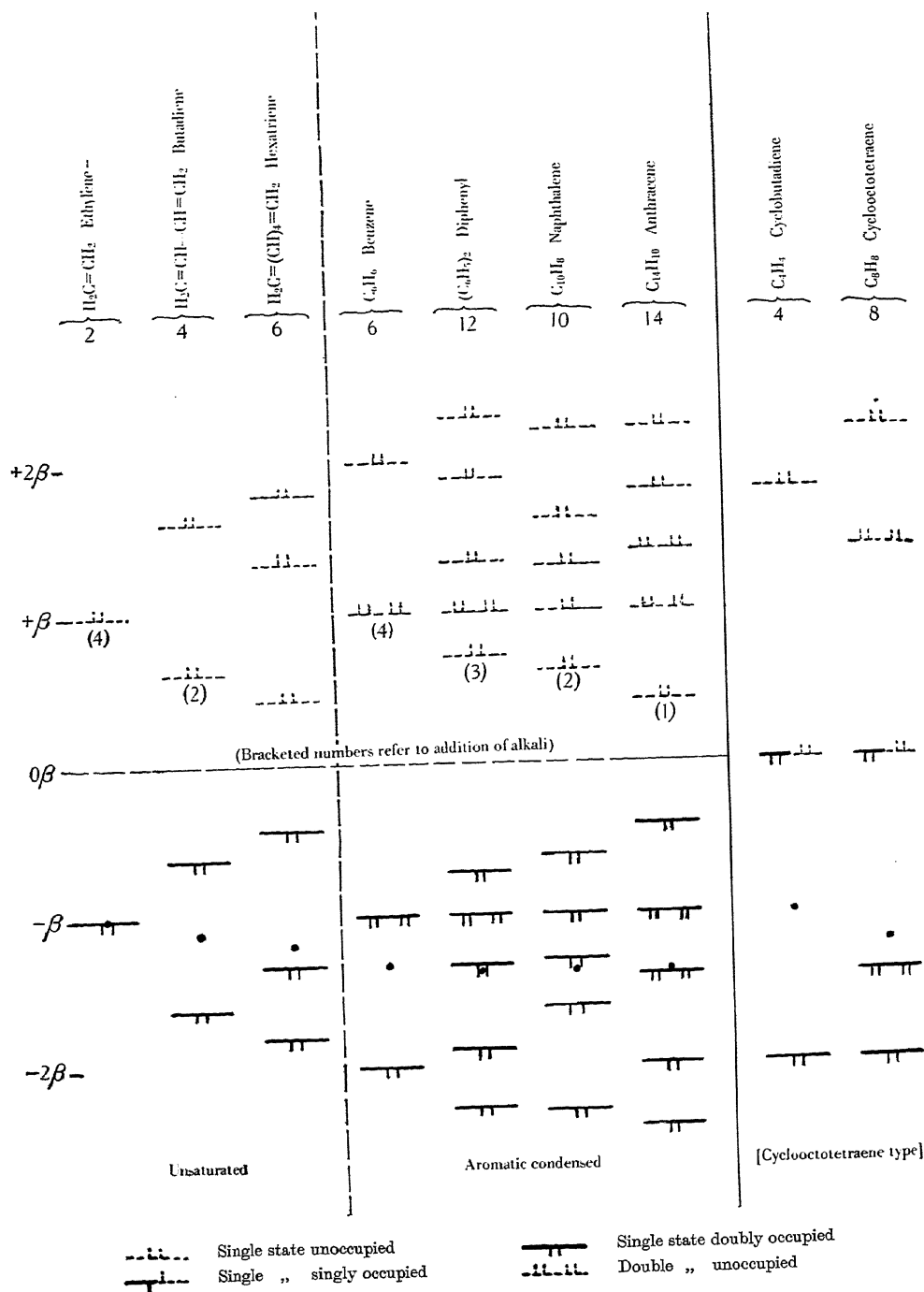


Figure 3



It will be seen that in contrast to the results of method I,  $E' - E$  always comes out  $> 0$ , in harmony with observation. In table 2 the values of  $\alpha\beta$  are given, which are obtained with  $\beta = 15$  or  $20$  k. cal./mol. respectively. The last two columns show that the values of  $(E' - E)$  are closely proportional to  $\alpha$ , and that with  $\beta = 20$ , we obtain satisfactory calculated values of  $E' - E$  and therefore of the actual energy content  $E$ . Naturally it is to be noted that the calculation by means of the binding constants entails some uncertainty (see for example cyclohexane, where  $E' - E = 15$  k. cal./mol., whilst  $E' - E$  should be zero). On the whole we can, however, conclude that method II gives results for the energy content which agree with the observations as well as can be expected from the basis underlying the calculations.

### (b) Free radicles

In general free radicles with "trivalent" C are not stable substances even if their individual molecules represent stable atomic arrangements. The reason for this is that by coalescence of two such radicle molecules, a chemical compound is produced which is formed with a large gain in free energy. This increase is in most cases of the order of the binding constant of a C—C linkage, and is therefore about 70 k. cal./mol.

There are, however (in solutions), certain radicles with "trivalent" C, which exist as stable substances or in a measurable dissociation equilibrium with their dimers. In every case where this is known, aromatic or unsaturated substituents are attached to the "trivalent" C-atom. In these radicles, the increase of free energy in dissociation of the dimers must be much smaller than for a normal C—C linkage. In fact Ziegler and Ewald\* found the heat of dissociation of hexaphenylethane into two triphenylmethyls  $(C_6H_5)_3C-C(C_6H_5)_3 \rightarrow 2C(C_6H_5)_3$  to be about 10 to 12 k. cal./mol. in different solvents. As opposed to this, the heat of activation for the decomposition, which proceeds as a monomolecular reaction, amounts to about 19 k. cal./mol. (at temperatures about  $0^\circ$  C.), and is therefore greater†.

The equilibrium degree of dissociation depends for different compounds on the aromatic or unsaturated substituents, and indeed the rule holds in general that the more bulky the substituent, the further to the side of the radicle lies the equilibrium point‡. Measurements of the heat of dissociation for radicles with trivalent C other than triphenylmethyl are not available up to the present.

Nothing need be said here as to the older attempts to interpret the stability of such radicles, which in any case led to contradiction§. (Theory of "valency requirements".) It need only be remarked that as early as 1928, Ingold|| gave an explanation which was based on mainly the same grounds as our theory, although it was not based on quantum theoretical calculations.

We illustrate the theory by the example of hexaphenylethane, on the basis of

\* K. Ziegler and L. Ewald, *Ann. d. Chem.* **473**, 163 (1929). (It is possible that these values are too low by a small amount, about 1 k.cal.)

† K. Ziegler, P. Orth and K. Weber, *Ann. d. Chem.* **504**, 131 (1933).

‡ W. Schlenk, T. Weickel and A. Herzenstein, *Liebigs Ann.* **372**, 1 (1910).

§ On this matter, see e.g. W. Hückel, *Theoretische Grundlagen der organischen Chemie.*

|| C. K. Ingold, *Ann. Rep. Chem. Soc.* **25**, 154 (1928); H. Brixton and C. K. Ingold, *Proc. Phil. Soc. Leeds*, **1**, 421 (1929).

method II. In contrast to the earlier attempts at explanation, the theory assumes that the C—C linkage which unites the two radicles in hexaphenylethane does not differ materially in structure from the normal C—C linkage. Rather it assumes that the small heat of dissociation is due to the fact that, during the process of separation of the radicles, the energy content of the two triphenylmethyls diminishes, so that the expenditure of energy necessary for the rupture of the C—C linkage is mainly provided by this decrease of energy content. This "gain of energy" is interpreted\* by quantum mechanics in the following manner. In hexaphenylethane, the four valencies proceeding from each of the middle C-atoms form a regular (or nearly regular) tetrahedral arrangement. The  $\pi$ -electrons of the phenyls attached to these two atoms cannot (or can only slightly) take part in the resonance coupling with the electrons of these C-atoms, owing to the symmetry of the eigenfunctions. When, however, the two radicles are separated, such a resonance is possible, and it is best from the energy point of view, when the radicle is plane. Then the electron which originally belonged to the C—C linkage has become a  $\pi$ -electron, and the plane arrangement is stabilized by the  $\pi$ -electron. Now the absolute value of the total resonant coupling in such an atomic arrangement is much greater than it is for three phenyl rings, whose  $\pi$ -electrons are isolated from each other in so far as resonance phenomena are concerned. Hence the gain of energy. The fact that the heat of activation is greater than the heat of dissociation† can easily be harmonized with this conception.

The increase of resonance energies can be taken from the data given in table 1. The total resonance energy of a single  $(C_6H_5)_3C$  before the dissociation is equal to that of three phenyls, i.e.  $-24\beta$ . After the dissociation, the resonance energy for a single triphenylmethyl is  $-25.794\beta$ . The gain per radicle is therefore  $1.794\beta$ , and for the two radicles resulting from the dissociation it is  $3.588\beta$ . With  $\beta = 15$ , this gives a gain of  $55.77$ , and with  $\beta = 20$ , a gain of  $71.76$  k. cal./mol. This increase is therefore in fact of the same order of magnitude as the work of separation of a C—C linkage. A quantitatively exact calculation of the energy of dissociation is not possible, since the structure of the  $\sigma$ -linkages proceeding from the central C-atom is changed in the dissociation, although the energy change concerned in these linkages will, it is true, be relatively small. On the other hand, the dependence on the substituents can be deduced with an accuracy corresponding to that with which  $\beta$  is known.

In general, the amount of energy which is gained by alteration of the resonance energy on the dissociation of a radicle we shall call the (static‡) "linkage demand" of the C—C linkage in the radicle, due to resonance of the  $\pi$ -electrons. If  $A_1$ ,  $A_2$  are these linkage demands for the two radicles into which the molecule splits, then  $A = A_1 + A_2$  is the total linkage demand of the C—C binding through resonance. Table 3(a) contains the values of  $A_i$  for a few radicles. They follow from the

\* E. Hückel, lecture at the Baden and Württemberg meeting of the Deutsch. Physik. Ges. Jan. 1933; *Z. f. Phys.* **83**, 632 (1933). (Based on method II.) Nearly simultaneously and independently by L. Pauling and G. W. Wheland, *J. Chem. Phys.* **1**, 362 (1933). (By method I.)

† E. Hückel, *Z. f. Phys.* **83**, 674 et seq. (1933).

‡ In contrast to a "kinetic" linkage demand which can be defined for the heat of activation, see E. Hückel, *loc. cit.*



resonance energies given in table 1, in the same way as for triphenylmethyl. Table 3(b) contains the values of  $A_i$  for some symmetrical aromatically and aromatic-aliphatically substituted ethanes. It is seen at once that in the completely aromatically

Table 3(a). Statical linkage demands  $A_i$  due to resonance in certain radicals

Radicle	$A_i = \alpha\beta$	$A_i$ in k. cal./mol., calculated for	
3 aromatic substituents:			
C (Diph) <sub>3</sub>	1.859 $\beta$	27.80	37.18
C (Diph) <sub>2</sub> Ph	1.841 $\beta$	27.62	36.82
C (Diph) (Ph) <sub>2</sub>	1.819 $\beta$	27.29	36.38
C (Ph) <sub>3</sub>	1.794 $\beta$	26.91	35.88
2 aromatic substituents: <sup>1</sup>			
C (Diph) <sub>2</sub> Aliph	1.351 $\beta$	20.27	27.02
C (Ph) <sub>2</sub> Aliph	1.200 $\beta$	18.00	24.00
1 aromatic substituent: <sup>1</sup>			
C (Diph) (Aliph) <sub>2</sub>	0.897 $\beta$	13.46	17.94
C (Ph) (Aliph) <sub>2</sub>	0.720 $\beta$	10.80	14.40
No aromatic substituents:			
C (Aliph) <sub>3</sub>	0 $\beta$	0	0

For brevity, the resonance energies for these radicals are not included in table 1.

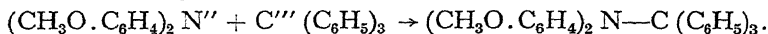
Table 3(b). Total linkage demand due to resonance,  $A = 2A_i$ ,  
for some symmetrically substituted ethanes

Compound	$A$	$A$ in k. cal./mol. calculated for	
		$\beta = 15$	$\beta = 20$
(Diph) <sub>3</sub> C—C (Diph) <sub>3</sub>	3.718 $\beta$	55.77	74.36
(Diph) <sub>2</sub> C—C (Diph) <sub>2</sub> Ph Ph	3.682 $\beta$	55.23	73.64
Diph C—C Diph (Ph) <sub>2</sub> (Ph) <sub>2</sub>	3.638 $\beta$	54.57	72.76
(Ph) <sub>3</sub> C—C (Ph) <sub>3</sub>	3.588 $\beta$	53.82	71.76
(Diph) <sub>2</sub> C—C (Diph) <sub>2</sub> Aliph Aliph	2.702 $\beta$	40.53	54.04
(Ph) <sub>2</sub> C—C (Ph) <sub>2</sub> Aliph Aliph	2.600 $\beta$	39.00	52.00
Diph C—C Diph (Aliph) <sub>2</sub> (Aliph) <sub>2</sub>	1.794 $\beta$	26.91	35.88
Ph C—C Ph (Aliph) <sub>2</sub> (Aliph) <sub>2</sub>	1.400 $\beta$	21.60	28.00
(Aliph) <sub>3</sub> C—C (Aliph) <sub>3</sub>	0 $\beta$	0	0
C (Ph) <sub>3</sub> → C (Ph) <sub>2</sub> + Ph	1.794 $\beta$	26.91	35.88

substituted ethanes, the linkage demand increases with the bulk of the substituent, i.e. the energy of dissociation diminishes. The difference, for example, between tridiphenylmethyl and triphenylmethyl amounts to 0.130 $\beta$ , which gives the value 1.95 with  $\beta = 15$  and 2.60 k. cal./mol. with  $\beta = 20$ . This is in harmony as regards

order of magnitude with the (not exactly known) difference between the dissociation constants of these compounds. Further, it can be deduced from table 3 that the substitution of only one aromatic substituent by an aliphatic one, reduces the linkage demand quite considerably, since this substituent can contribute nothing to the increase of resonance energy. This explains why stable free radicles are known only in completely aromatic or aromatic-unsaturated substituted C-atoms\*. We see also, that radicles like allyl,  $\text{CH}_2\text{—CH—CH}_2$ , for example, cannot be stable. For the gain of resonance energy in the dissociation of the dimers is here much too small ( $A = 2 \times 2.82\beta - 2 \times 2\beta = 1.64\beta$ ). Finally, in table 3(b), the linkage demand for dissociation of tetraphenylmethane is surveyed from the point of view why the dissociation does not take place, which the older theories of valency requirements could not explain. Here it appears that in the dissociation of a  $\text{C—(C}_6\text{H}_5)$  linkage, only one of the resulting radicles gains resonance energy; in other words, that the linkage is only "unilaterally demanded."

The theory can also remove other contradictions which were inherent in the older conceptions†. It is known that certain free radicles with trivalent C, and others with divalent N, each of which is stable by itself, i.e. the dimers of which tend to dissociate, will yet combine with each other, e.g.



The theory of valency requirements was not able to explain this. On the other hand, this behaviour fits naturally into our theory. If we represent the work of separation of the corresponding substitution bonds by  $(\text{C—C})$ ,  $(\text{N—N})$ ,  $(\text{C—N})$ , then the conditions for the observed behaviour are expressed by

$$(\text{C—N}) > (\text{C—C}); \quad (\text{C—N}) > (\text{N—N}); \quad (\text{N—N}) \leq (\text{C—C}).$$

(The latter because the dimer of the nitrogen radicle is at least as strongly dissociated as hexaphenylethane.) Here experimentally  $(\text{C—C}) \cong 11 \text{ k. cal./mol.}$

If further we denote the work of separation of the linkages, without taking account of the gain of resonance energy, by  $(\text{C—C})_0$ ,  $(\text{N—N})_0$ ,  $(\text{C—N})_0$  and the linkage demands for the two radicles by  $A_C$  and  $A_N$ , then

$$\begin{aligned} (\text{C—C}) &= (\text{C—C})_0 - 2A_C \\ (\text{N—N}) &= (\text{N—N})_0 - 2A_N \\ (\text{C—N}) &= (\text{C—N})_0 - (A_C + A_N), \end{aligned}$$

and the above conditions become

$$\begin{aligned} (\text{C—C})_0 - (\text{C—N})_0 &< A_C - A_N \\ (\text{C—N})_0 - (\text{N—N})_0 &> A_C - A_N \\ (\text{C—C})_0 - (\text{N—N})_0 &\geq 2(A_C - A_N). \end{aligned}$$

If we take the linkage demands  $A_C = 1.794\beta$  and  $A_N = 1.200\beta$  (the latter is the value for a radicle  $\text{C(Ph)}_2 \text{ Aliph.}$ ; the actual linkage demand is possibly smaller),

\* Whether the radicles with an aliphatic substituent like  $(\text{C}_6\text{H}_5)_2\text{C—CH}_3$ ,  $(\text{C}_6\text{H}_5 \cdot \text{C}_6\text{H}_4)_2\text{C—CH}_3$  observed by Conant and his collaborators are really stable, seems to us not definitely proved. (Cf. W. Hückel, *Theoret. Grundl. der org. Chemie*, 2nd edition, 1, 116, Leipzig (1934). Also J. B. Conant and N. M. Bigelow, *J. Amer. Chem. Soc.* 50, 2641 (1928), and J. B. Conant and R. W. Schultz, *ibid.* 55, 2098 (1933).)

† This was pointed out by Pauling.

and if we take, for the work of separation, the binding constants  $(\text{C}-\text{C})_0 = 72.6$ ,  $(\text{C}-\text{N})_0 = 68$  and  $(\text{N}-\text{N})_0 = 32$ , then with  $\beta = 17.5$ , all the requirements are fulfilled. There even remains a rather large margin for a change in the assumed values.

As mentioned above, Pauling and Wheland explain the stability of the radicles under discussion in practically the same way. They calculate only the energy increase which occurs in the dissociation by method I and interpret it then as a gain in "exchange energy." (They speak of a gain of "resonance energy," but this expression is to be differently interpreted than in method II; the exchange energy alters during the dissociation and we may describe this as an alteration of the "resonance" between the canonical structures.) In the calculation of this increase according to method I, they have indeed to simplify the procedure in a somewhat arbitrary fashion, owing to the extremely great number of canonical structures\*. They find the right order of magnitude for the linkage demand, but a much greater dependence on the bulk of the substituent than can be reconciled with observation†. For example, they obtain a difference of 11.8 k. cal. between the heats of dissociation of hexaphenylethane and hexadiphenylethane, which is certainly much too great in view of the observed difference in the degree of dissociation.

The same cause, which we used to explain the small work of dissociation of two aromatic-substituted C-atoms, can also be made to explain why the heat of the transformation, Diamond-graphite, is so small. In the diamond-graphite transformation, half a diamond linkage is broken per C-atom. Consequently there results one  $\pi$ -electron for each atom in graphite, and the  $\pi$ -electrons in the individual slip planes of the graphite undergo resonance. The calculation of this coupling by method II for a single slip plane gives a continuum as the term spectrum for these electrons. One half of the states is binding, the other relaxing, by resonance. In the ground state, all the binding states are doubly occupied. The linkages cannot be localized. Within the lattice plane, the electrons have the character of conduction electrons. As mean resonance energy for a  $\pi$ -electron, we find  $-1.58\beta$ . If the work of separation per C—C linkage is taken as about 73 k. cal., then it must be taken as about 36.5 k. cal. per C-atom. On the other hand resonance energy is gained. With  $\beta = 15$ , this gain is calculated as 23.7, or with  $\beta = 20$  as 31.6 k. cal./mol. It agrees therefore in order of magnitude with the work expended. Naturally, this is only quite a rough estimate, since:

(1) If the structure of the  $\sigma$ -linkage changes in the transformation, this will contribute to the energy change, and will be of relatively more importance than in the substituted ethanes.

(2) After the transformation, forces—although rather weak ones—still act between the slip planes, which depend on van der Waals' forces and on residual valencies. (Resonance action between the  $\pi$ -electrons of adjacent lattice planes.)

\* This simplification consists in the main in the neglect of the "excited" structures, i.e. those for which non-adjacent atoms are connected by valency links.

† In the original work, incorrect values were obtained at first. The value 11.8 k. cal. given here is taken from a correction given by Pauling and Wheland. [Note added in proof: For this correction see L. Pauling and G. W. Wheland, *J. Chem. Phys.* 2, 482 (1934).]

(3) The value of  $\beta$  in graphite may deviate from the value deduced from the energy contents of the aromatic compounds.

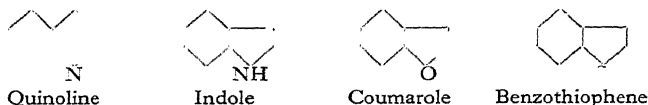
It would not be easy to take these points quantitatively into account, but it does not seem open to doubt that the conceptions developed here roughly deal with the essentials.

(c) *Discussion of chemical properties in relation to constitution*

The results of method II yield certain qualitative conclusions on a number of chemical properties. We consider first *Ring compounds, diphenyl and condensed systems*. From figure 3 it will be seen that the ring with 6 members, diphenyl and condensed systems, all differ from rings with 4, 8; 5, 7 members in that in the former compounds all  $\pi$ -electrons are in binding states which are fully occupied. We have here, therefore, closed electron groups. On the other hand, the 4 and 8 ring compounds have two electrons which neither bind nor separate, and also the highest occupied state, which is doubly degenerate, is not fully occupied. However, it is very improbable that in either of these rings the calculated electronic structure can have a real significance, since in them probably the atoms are no longer arranged in a plane, on account of the great deviation of the valency angles from  $120^\circ$ , which would be necessary for a plane structure. Consequently we shall not consider these rings further. (In any case, the 4 ring is unknown.) The 5 and 7 rings have no closed electron groups, and indeed in the 5 ring a binding state to close the group is lacking, whilst in the 7 ring a single electron is in a non-binding state. This accounts for the fact that the 5 ring, at least in the presence of a positive ion, has a tendency to take up one electron, which results in the existence of metal compounds like  $[\text{C}_5\text{H}_5]\text{-K}^+$  which are considered as of ionic character, whilst in the 7 ring no such compounds are known. Among the rings, the 6 ring is specially distinctive. This individuality exists also among heterocyclic rings. This arises, however, not on account of the number 6 of atoms in the ring, but on account of the number 6 of  $\pi$ -electrons. Such heterocyclic rings are, e.g.\*



Corresponding to these we have, for example, the heterocyclic condensed ring-systems



which are analogous to naphthalene.

In these compounds, N brings *one*  $\pi$ -electron, NH, O and S bring two  $\pi$ -electrons into the ring, and the total number of 6 or 10 electrons forms a closed electron group. (In the corresponding compounds analogous to anthracene the

\* For further details, see W. Hückel, *Theoret. Grundl.* 2nd edition, 1, 386, Leipzig (1934).

critical number is 14.) Naturally, the symmetry of the eigenfunctions and the eigenvalues of the  $\pi$ -electrons are distorted in these cases, though this does not affect the enumeration of the binding states. A quantitative treatment of such compounds has not yet been attempted.

The difference in behaviour between aromatic and unsaturated compounds is not easy to interpret, since the latter also have closed electron groups (see figure 3).

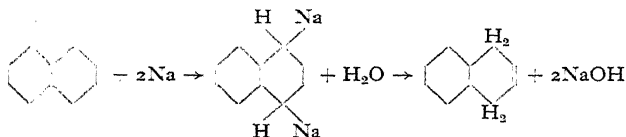
In free radicals, the highest state is not fully occupied, and indeed this state can be:

- (1) Neither binding nor relaxing (allyl, etc.; triphenylmethyl, etc.).
- (2) Binding [ $C_3H_3$ ,  $C_5(C_6H_5)_5$ ].
- (3) Relaxing ( $C_7H_7$ ).

The stable radicals like triphenylmethyl have on the one hand a tendency to gain an electron (forming a metal compound like  $(C_6H_5)_3C^- Na^+$ , which is liable to dissociate into the ions  $(C_6H_5)_3C^-$  and  $Na^+$ ). On the other hand, they have also a tendency to lose an electron (forming compounds like  $(C_6H_5)_3C^+ Cl^-$ , which is liable to dissociate into  $(C_6H_5)_3C^+$  and  $Cl^-$ ). These radicals therefore exhibit a behaviour which can be described as amphoteric.

The radicle  $C_3H_3$ , which is not stable in itself, has no tendency to behave as a positive ion (its chlorine compound has no ion-forming character), corresponding to the fact that the highest occupied state is binding. On the contrary, as already mentioned, it forms compounds in which it can be regarded as a negative ion. It has therefore an electro-negative character. The stable pentaphenylcyclopentadienyl should also possess such a character, since in it also, the highest occupied state is binding, and it is one electron short of a closed group. Although as far as we are aware, there are no data on the electrochemical character of this radicle, we can refer to the fact that Ziegler\* from other considerations concludes that this radicle should have a pronounced electro-negative character.

Some of the molecules with closed electron groups have, when alkalis are present, a tendency to take up electrons. They are to a greater or less degree in a condition to take up alkali metals, and then to become hydrogenated. Thus:



The ease with which the addition of one and the same alkali metal takes place, decreases in the following sequence. (The data are only qualitative.)

Anthracene easily adds Na and Li in the 9, 10 position.

Naphthalene adds Na slowly and Li faster, in the 1, 4 position. Conjugated double bonds (isoprene) add them in the 1, 4 position; Na about as fast as naphthalene, Li not investigated.

\* K. Ziegler and B. Schnell, *Ann. d. Chem.* **445**, 266 (1925).

Phenanthrene adds Na very slowly, Li somewhat slower than naphthalene.

Diphenyl in the 1, 4 position\*, adds Li but not Na.

Benzol and isolated double bonds add neither Na nor Li. Finally diphenylpolyenes add Na to the C-atom which is next to the phenyls, and do so rather easily. (One deduces the position of the addition, from the constitution of the products formed by hydrogenation, assuming that the hydrogenation occurs at the same place as that at which the metal is added.)

It now seems that there is a connexion between the sequence for ease of addition, and the sequence of resonance energies in the lowest unoccupied states (which can be doubly occupied!). This may be seen from figure 3, where the compounds are numbered according to the latter sequence. (Phenanthrene was not calculated. Diphenylpolyenes should also combine easily.) Moreover, there is a relation between the positions at which the addition occurs, and the charge distribution of the lowest unoccupied states, which in the presence of alkalis are occupied. The addition occurs namely in that position where this charge distribution has its maximum. This is so for all the cases mentioned where the calculation of the charge distribution has been carried out (anthracene, naphthalene, conjugated double bonds, diphenylpolyenes) with the exception of diphenyl. Here the greatest charge density is at the 4, 4 position, and we should therefore anticipate that the addition would occur at these points. In naphthalene, the charge density is the same at the positions 1, 4 and 5, 8. That the hydrogenation occurs only at the 1, 4 (or 5, 8) and not in (1, 8) or (4, 5) may be connected with the fact that for the latter case the resulting compounds have less favourable energy, and thus rearrange themselves to form 1, 4 dihydronaphthalene.

## § 6. CONCLUSION

As already mentioned, I have shown that a quantum-theoretical explanation can be given using method II, for the individual reactive behaviour of substituted benzenes ("induced polarities"). Consequently nothing further will be said here on this point. The relevant original work may be consulted†.

In general the theory has been so far developed that the employment of only one constant, the resonance integral  $\beta$ , is required. It is clear that with these limitations, only relatively rough conclusions as to the constitution and behaviour can be drawn. I believe, however, that I have shown that quite important progress has already been made towards the understanding of the compounds under consideration. On points for which a closer examination, which naturally must be much more complicated, would be necessary, I have given references at different points of the above outline.

The treatment of further properties, such as magnetism and light absorption, is a task for further research.

\* According to W. Schlenk and E. Bergmann (*Ann. d. Chem.* **463**, 1 (1929)) the addition should at least occur in the same phenyl, probably in the 1, 4 position. The argument for this seems to us not very cogent.

† E. Hückel, *Z. f. Phys.* **72**, 310 (1931); see also *Nature*, June 25, 1932.

# DESCRIPTION OF THE BINDING FORCES IN MOLECULES AND CRYSTAL LATTICES ON QUANTUM THEORY

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**ABSTRACT.** The distinction between heteropolar and homopolar bonds is briefly outlined. As regards the theoretical explanation of the phenomena we may obtain different degrees of a theory of cohering matter, according to the extent to which quantum theory is introduced into the basis of the theory.

A number of problems are then taken up in order.

(1) Why is hydrogen diatomic? To explain this it is necessary to show that when a number of electrons and a number of protons are brought together, the state of lowest energy is that in which the protons are associated in pairs, at a fixed distance apart, and that two electrons are associated with them. Various methods of approximating to the solution of the mathematical problem involved are discussed, and it is emphasized that all of them rest on "models."

(2) Why is  $\text{H}_2\text{O}$  bent, and indeed why is such an angle characteristic of a large group of oxygen compounds? The discussion of this problem leads to a consideration of the distinction between a valency link binding and a (homopolar) binding not describable by valency links.

(3) Why is Na a metal, but Cl a gas, although both are univalent? Under this heading are discussed, among other points, the conditions which favour lattice formation as a state of lowest energy.

(4) Why do solid insulators occur, like the diamond? In other words, the problem is that of explaining the existence of non-ionic lattices with strong binding.

(5) How are the transition cases like arsenic to be classified?

Finally, it is pointed out that we cannot yet calculate in general when Nature will use one sort of binding, and when the other. Consequently a survey of the types of aggregation actually met with in the elements is of interest, and a diagram showing this is provided.

## § 1. EMPIRICAL

To obtain a concise survey of the *cohesive properties of matter in bulk*, we will arrange the simple substances with respect to the strength with which they cohere and to other obvious properties.

The quite coarse classification into those substances which at ordinary temperatures are solid and those which are gases (among simple substances, only water and mercury are liquid) shows two great groups of forces which hold together the lattice of the solid state. If we include electrical conductivity as noteworthy, we obtain the following schematic survey:

	Examples	Melting point	Solid state	
Rare gases	He, Ne ...	Very low	Insulators	Atomic lattice
Polyatomic gases	H <sub>2</sub> , N <sub>2</sub> , O <sub>2</sub> F <sub>2</sub> , Cl <sub>2</sub> , ... CH <sub>4</sub>			Molecular lattice
	CO, CO <sub>2</sub> HCl, H <sub>2</sub> O, NH <sub>3</sub>	Low		
Salts	LiF, ... CsI, MgO, ... CaF <sub>2</sub>	High	Insulators to electrolytic conductors	Ionic lattice
Metals	Na, Mg, Al...Fe ScN, TiC	.....	Metallic conductors	Atomic lattice
Compounds of the nature of the diamond	Diamond, Si, B? SiC, BN	Very high	Insulators	

To those properties of the simplest substances collected in the table, we have to add the general system of ideas which chemistry has abstracted from its enormous empirical material. As limiting cases between which there are transitional cases, we have heteropolar and homopolar bonds. Heteropolar compounds in the ideal case form solid bodies at ordinary temperatures (we do not consider here the case of solutions). A characteristic integer can be attached to the individual atoms and it may be either positive or negative. In compounds, the sum of these numbers is zero even in a comparatively small region. In addition it would seem that the atomic arrangement in the crystal lattice is mainly determined by the relative "sizes" of the atoms. If we extend our considerations to cases like NaCl vapour, or (more remote from the ideal case) HCl and NH<sub>3</sub> gas, then we find molecules; in them the atoms are so constituted that the sum of the characteristic numbers (to call them valency numbers departs probably from the language of the chemist) is zero.

In homopolar compounds, which form molecules in the simple cases, the atom has a valency number, an integer which has no sign; multiple valencies of an atom have fixed directions to each other (tetrahedral for the C-, plane angle for the O-atom). "The valencies saturate each other mutually," a valency from one atom combining with a valency from a neighbouring atom to form a valency link.

## § 2. THEORETICAL BASIS

The atom as a stable dynamical system of charged particles is inexplicable to classical physics. According to the extent to which we apply quantum theory, whether we only introduce general facts of the quantum theory, and think, in the main, on classical lines, or whether we employ complete quantum mechanics for the phenomena, we obtain *different degrees of a theory of cohering matter*.

As a first and rather crude step we consider atoms as given and assume forces between them, repulsive on account of the impenetrability, attractive on account of the electrical structure of the atom. To this stage belongs the classical kinetic theory



of matter, van der Waals' explanation of the relation between the liquid and gaseous states, and Debye's explanation of the constants in van der Waals' equation. This step in the theory did not explain the special properties of different substances, nor, above all, the rules of chemistry.

At a more advanced stage the individual properties of atoms, such as the existence and energy of positive or negative atomic ions, are deduced from the quantum theory of the atom. The aggregation of matter is then explained as being due to the electrostatic forces between the ions, so that the explanation is classical and pictorial. To this stage belong Kossel's explanation of heteropolar chemistry and Born's theory of the atomic lattice. The chief points left unexplained are homopolar molecules, metals, and certain solid insulators like diamond.

In the third stage, the quantum theory of the molecule and the crystal lattice, electrons are regarded as moving in a system of a few nuclei (as in molecules) or of many nuclei (as in crystal lattices) in a non-classical and non-pictorial manner by the methods of the (non-relativistic) quantum mechanics initiated by Heisenberg and Schrödinger (1925-26). This stage of development leaves most of the results of the earlier stages untouched; however, it adds some new results, and explains the properties of aggregated substances which are not explicable on classical, pictorial lines, viz. homopolar chemistry and solid atomic lattices (metals, and substances of the diamond type).

### § 3. THEORY OF HOMOPOLAR BINDING IN MOLECULES AND CRYSTALS

We illustrate certain important features of the theory by examples.

*Why is hydrogen diatomic?* In order to explain the diatomic nature, we must calculate that the energy of the lowest state of a system of two electrons in the field of force of two rigidly fixed H-nuclei has a minimum at a certain finite separation of these nuclei. Further we must calculate that the energy of the lowest level of a system of three electrons in the field of force of three rigidly fixed H-nuclei has a minimum when two of the nuclei have a certain fixed distance, and the third is remote from them. Heitler and London calculated out the system with two nuclei by an approximation method which started from the ground state of two separate atoms each with one electron. The principal feature is the classically unexplained splitting of the energy into two energy levels (i.e. terms), as we proceed from widely separated to closely approaching nuclei. In this process, one of the terms goes to lower values, and finally reaches a minimum, whilst the other tends upwards. London studied the addition of a third atom to this assembly: the lower energy level does not split further; there is no means for the energy to decrease further on closer approach of the third nucleus. The valencies of both original atoms were "saturated," giving rise to a condition which led to no further splitting.

Another method of studying the same problem is the following: we can obtain approximately the condition of a single electron in the field of force of two or more nuclei by a kind of interpolation between the states for widely separated nuclei (when the electron behaves as the atomic electron near one nucleus) and

for slightly separated nuclei (when the state of the electron may be approximately obtained from the state in an atom, whose nuclear charge originates from coalescence of the nuclei). The lowest state of the single electron is diminished on bringing together the widely separated nuclei. The state of a system with many electrons is in this method approximated through the states of the individual electrons (this is also the route by which the atomic spectra were first understood). Then according to Pauli's principle, every (non-degenerate) state contains at the most two electrons. Thus in  $H_2$ , two electrons can be brought into the lower level; in  $H_3$ , one electron would have to be in a higher energy state (compare the relations in the He- and Li-atoms).

Both these concepts of binding in  $H_2$  and of saturation have been generalized: the former to the spin-valency theory of London, Heitler and others, and by a further refinement of Slater's, whilst the latter has been extended to questions of chemical binding by Herzberg and Lennard-Jones. The method (a) of spin valencies, which builds the proper functions of the ground level of the molecule out of the proper functions of the ground levels of the individual atoms (not the individual electrons of this atom), shows which characteristics of the quantum mechanical description correspond to the concepts of "valency number" and "saturation." Slater's method (b), which builds the proper functions of the ground state of the molecule out of the proper functions of the individual electrons in the atom, can deal with cases which are too complicated for treatment by method (a). It brings out criteria of the quantum mechanical description which correspond to the chemical concepts of "valency angle" and "valency bond." Methods (a) and (b) (which do not differ in this matter) are applied by Heisenberg to the explanation of ferromagnetism on quantum theory.

Method (c), which builds the proper functions of the lowest state of the molecule out of the proper functions of the individual electrons in the field of force of this molecule, may not be so accurate, but is essentially simpler than Slater's method. It also embodies a quantum-mechanical description of the valency angle and valency bonds. It can be applied to the treatment of many properties of crystal lattices, especially metals. Its simplest form is then Sommerfeld's conception of free electrons. A more general form is Bloch's treatment of single electrons in periodic fields of force. In that case, the proper functions of the individual electrons are waves with a propagation vector  $k$ . If the energy of the state of the single electron can be approximated in the form  $E = \frac{1}{2m'} k^2$  (and this is often the case), then  $E = \frac{m'}{2} v^2$ , where  $v$  is the "group velocity"; in this case the system of electrons can be treated as a system of free particles with an "apparent" mass  $m'$ .

All three conceptions rest on "Models," i.e. on simplified statements of the properties of actual molecules. Properties which in themselves are not negligibly small, but which are not important for the phenomena treated, are left aside.

*Why is  $H_2O$  bent?* The theory of heteropolar bindings could explain such an angle as due to the polarizability of the O-ion, but not the appearance of such an

angle as a general characteristic of a large group of O-compounds. Slater and Pauling showed by means of the above described method (b) that the quantum theory of homopolar molecules also leads to a (probably corresponding) understanding of this angle (as a property of the valencies of the O-atom). The angle can also be explained by method (c): let us take two nuclei, which individually can take up an  $s$ -electron in the lowest state, and an atom residue which possesses two  $p$ -electrons in the lowest state ( $p^2$ , so that instead of the two  $p$ -“gaps” of the O-atom we take two  $p$ -electrons), then it can be shown that in the “straight” arrangement  $s \dots p^2 \dots s$ , only one energy level (which can hold two electrons) of lowest energy occurs. The two further electrons must enter a higher state. With the “bent” arrangement  $s \nearrow p^2 \searrow s$  on the other hand, there are two neighbouring conditions of low energy for the four electrons, with approximately the same energy. With only a very slight alteration of the description, we obtain two coincident energy states for the single electrons; the proper function of the one differs appreciably from zero at the middle atom ( $p^2$ ), at one of the end atoms ( $s$ ) and between the two ( $s-p^2$ ); that of the other differs appreciably from zero at the middle atom, at the other end atom and between the two. This state of affairs is the quantum mechanical description of the two valency links. In our example, the binding with valency links is describable in the sense of the quantum theory for the bent arrangement but not for the straight. If the  $p^2$  atom enters with both its valencies into a combination which is describable with valency links, and in which  $s$ -atoms are attached at the ends of the links, then the latter must form an angle.

Slater's treatment, and that sketched above by method (c), provide a *quantum mechanical description of valency links*. From the point of view of method (c), a connexion with valency links is made when the proper function of the ground state of the molecule is approximated by such proper functions of the individual electrons as are only appreciably different from zero between and at two neighbouring atoms. Every orbital of an electron described by such a proper function is doubly occupied. On account of the model character of our representation, we cannot generally prove that a state of a molecule (or of a crystal lattice) described by valency links is always the lowest energy state. For an estimate which shall show that the bent state of  $\text{H}_2\text{O}$  with valency links has lower energy than the deepest state of a straight  $\text{H}_2\text{O}$  whose proper function is described otherwise, doubtful simplifications must be made. We must not be surprised if Nature in some cases which are analogous to our example shows us bindings which are not describable by valency links. In fact, these occur, as the binding in metal lattices shows; also the benzene ring, aromatic rings in general, and the graphite lattice are examples of structures not describable by valency links. The “*valency link binding*,” as we will call the above-described types, is therefore a concept exactly describable by quantum mechanics. How far Nature utilizes it, we cannot always calculate. The other kind of homopolar binding, where, in method (c), the proper functions of the individual electrons cannot be so constructed that they belong to two neighbours, obtains its *binding energy from the same unpictorial and non-classical features of the*

*theory*, and is therefore closely related to the valency link binding. The energies are also of the same order of magnitude. Differences in other respects (conductivity of metals, certain properties of the aromatic ring), justify, however, a conceptual difference between a valency link binding and a (homopolar) binding not describable by valency links.

*Why is Na a metal and Cl a gas?* The wholly different ways in which Na-atoms and Cl-atoms (at low and ordinary temperatures) become aggregated in the material in bulk, although they are both monovalent atoms, is an example of the fact that Nature utilizes the possibilities of valency link binding as well as the other homopolar possibility. The quantum mechanical treatment had to compare the model of a system of electrons in the field of force of the same number of regularly ordered (maybe space-centred cubic) atomic residues with charge  $+e$ , with the model where these electrons moved in the field of force of neighbouring pairs of residues, which otherwise were at great distances from each other. For the low terms, in contrast to the case of individual free atoms, the deviation of the quantum mechanics from the classical mechanics is important in both cases, as the Heitler-London calculation of the term separation for  $H_2$  or the possibility of interpolation of the electron term in the molecule between two atomic states, showed earlier.

The large number of neighbours which an atom has is favourable to the lattice—in the normal metal, an atom has twelve or eight neighbours (fourteen if we include those only slightly farther away). For the molecule, it is favourable that a valency link should give a greater contribution to the binding than a pair of neighbours in the lattice. Since our approximation methods are of no further use for the distance relations which actually occur, the deductions must remain qualitative; we cannot therefore show deductively, why Na forms a solid lattice and Cl forms molecules. Yet there are certain circumstances which seem to favour the lattice arrangement in Na rather than in Cl. The *s*-proper functions of the Na-atom, on account of their spherical symmetry, can better utilize the advantage of the neighbours on every side than the *p*-“gaps” of the Cl-atom.

*Why do solid insulators with atomic lattices occur, like the diamond?* For the electrical conductivity of metals, it is important that a continuum of terms should belong to the lowest state of the multi-centred system corresponding to the lattice, and that at indefinitely small departures from the ground term there should be states which produce an electric current. Lattices composed of saturated molecules and of ions of rare-gas type are insulators, since the ground term is a single and isolated one. To understand the existence of non-ionic lattices with strong binding, we must show that in other cases the ground term of the crystal can be a single and isolated one. In method (c) this follows from the fact that the levels of the individual electrons, which form a continuum, have a finite gap exactly at the place up to which the states are occupied.

We can make this clear by a one-dimensional model. The electrons of the atoms, of which the chain lying in the  $x$  direction is to consist, are to be in *s*- and *p*-states. The *s*-proper functions are symmetrical with respect to the nuclei, in their dependence on  $x$ , whilst the *p*-proper functions are antisymmetric (figure 1).

We shall assume an  $s$ - and a  $p$ -state to be neighbours on an energy scale; we exclude degeneration of the  $p$ -state itself. With this simplification, the "periodic system" of the elements has periods of four, and consequently four electrons can be brought into the  $s$ - and  $p$ -states of a level. If we consider now the individual electrons in the complete chain system, as far as they are built out of the  $s$ - and  $p$ -states considered, we obtain the scheme shown in figure 2, for the energy of the individual electrons, as a function of a quantum number  $k$ , which is connected with the translatory properties of the chain (as shown by Bloch). When considering solely the  $s$ -states or the  $p$ -states of the separate atoms, the dotted curves were obtained (Bloch's curves) for the electrons of the chain, but taking both into account, the continuous curves are obtained. Each of the curves contains as many states as the chain has atoms; according to the Pauli principle, twice as many electrons can occur therein. The lower states of the individual electrons (roughly speaking, those in the lower curve) contribute to the binding, and those in the higher states tend to relax it.

If each atom of the chain brings an electron with it, half the states of the lower curve are occupied (figure 3a); we obtain *binding*. The limits up to which the states are occupied lie (for a chain with many members) in a continuum. If every atom of the chain brings two electrons with it, plainly the lower curve is fully occupied (figure 3b); we obtain *strong binding*. In this case it is not possible with a small expenditure of energy to produce another distribution of electrons. We have therefore an *insulator*, whose properties correspond to those of the diamond. If every atom brings three electrons, then half the upper curve is also occupied (figure 3c); the strong binding is relaxed again; in this case we have a *metal*. When every atom is accompanied by four electrons, the upper curve as well as the lower is fully occupied (figure 3d); we have an *insulator*. Moreover, the binding is yet further relaxed. We obtain, as would be expected, the loose lattice of a "rare gas."

When we attempt to extend the model to more dimensions, we see that for the occurrence of states in the insulator with strong binding, it is important that the binding in its lattice should be interpretable as valency link binding. According to their lattice structure and the valency numbers of their atoms, diamond, Si, SiC, Ge, one form of Sn, and BN belong to this class. As transition cases in this neighbourhood, lie some of the modifications of As, Sb, Bi, Se and Te. That some of these are metals is due to the fact that the relations of the model are disturbed by other terms, and is (especially for the higher atomic numbers) not to be wondered at.

*How are the transition cases As, Sb, Si, Se, Te to be classified?* We shall generalize our model of the uni-dimensional chain somewhat in that, by utilizing the  $y$ -direction, we place at the disposal of the electrons of the individually separated atoms, one  $s$ - and two coincident  $p$ -states. The  $s$  will be spherically symmetrical, one of the  $p$ -proper functions ( $p_x$ ) will have a node perpendicular to the  $x$ -direction, the other ( $p_y$ ) will result from it by rotating the  $x$ -direction to the  $y$ -direction. A period of the "periodic system" of the elements will then comprise six atoms; the rare gases are first reached when the atom has six electrons. The term scheme of the electrons in the chain is then that of figure 4. The newly added curve corresponds to the  $p_y$ -

states. It can happen that its lowest point lies above or below the highest point of the lower curve. In every case, if each atom is accompanied by one electron, we obtain a *metal*. If each atom brings with it three, four or five electrons, we also obtain a *metal*; the binding strengths diminish with four and five electrons. If every atom is responsible for six electrons, we obtain a loose *rare-gas lattice*. In the case where there is a gap between the middle and lower curves, we obtain, if each atom brings with it two electrons, an *insulator with strong binding forces of cohesion*

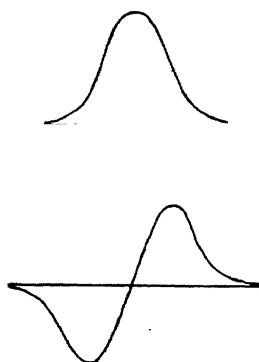


Figure 1. *s*- and *p*-proper functions of the model.

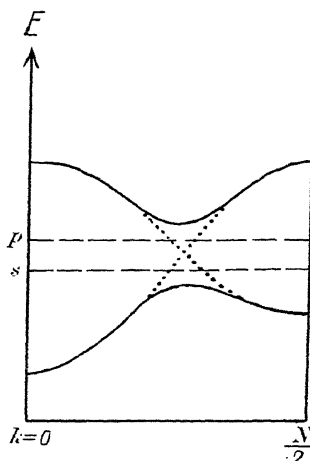


Figure 2. (From Hund, *Z. f. Phys.* 74, 7 (1932).) Energy values of the model.

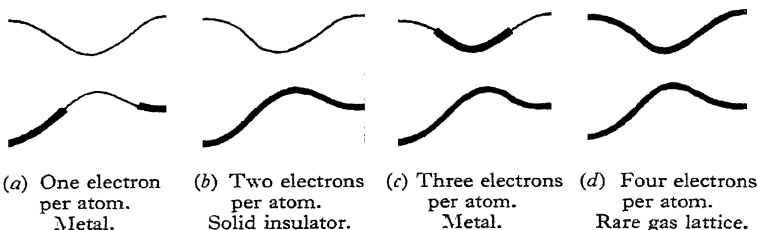
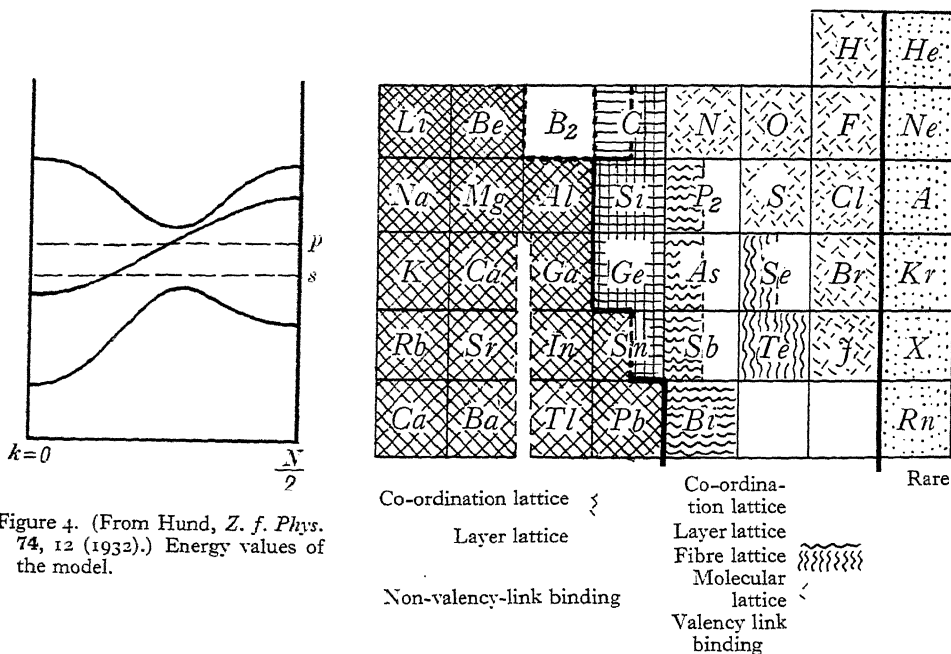


Figure 3. (From Hund, *Zs. f. Phys.* 74, 8 (1932).) Occupied states of the model.

(if the gap is small, the substance is a semi-conductor). In the case where the energy range of the middle curve overlaps that of the lower, there is, if every atom is accompanied by two electrons, a part from the lower area which remains free, and from the middle one a part which is occupied. We obtain a *metal with peculiar properties*. For cohesion, the overlap, if it is not too big, is without effect; it can therefore be described with reference to the states of the lower curve alone (valency link binding). The conduction properties can be so described, that the middle region has certain conduction electrons, and the lower region certain gaps, which in many respects behave like conduction electrons.

The application of the model to three dimensions shows that for the transition cases between an insulator with strong binding and a metal, it is important that the lattice should be representable as a valency link lattice (that therefore each atom should have as many outer electrons as there are valency links proceeding from it) but that for the electrons of the atom, states should be available, which do not enter into the valency link binding. The lattices of As, Sb, Bi seem from their structure to belong to this type. They may be so represented that every atom is connected by just one valency link to its three nearest neighbours. The three valencies proceed, not from



three outer electrons, but from three gaps. We will however, for simplicity, speak of electrons. The valency angles are explained because the valency links can be described by means of the proper functions of the three  $p$ -states (in Slater's sense, or in that of method (c)). Now we can, in addition, form proper functions of the electrons in the lattice from the proper functions of the  $s$ -states. It appears that these energies overlap somewhat the energies of the valency link states, so that some of the former are occupied, and some of the latter unoccupied. It is probably because of this that many properties of bismuth are only explicable if we assume a very small number of free electrons.

## § 4. SURVEY OF THE TYPES OF BINDING IN THE ELEMENTS

We cannot calculate quantitatively when Nature will make use of one kind of strong homopolar binding (for which a description must use non-classical methods)—i.e. valency link binding—and when she will use the other. A collection of the relations actually found is interesting. Figure 5 gives a survey of the combinations in the elements, and therefore in aggregated material consisting of unmixed similar atoms. In the usual arrangement of the periodic system of the elements, the groups Sc to Zn, Y to Cd, La to Hg are neglected; they should not be differentiated from their surroundings in type of binding. On the “left” side we have the type of binding not to be described with valency links; on the “right” side, the valency link binding. Sub-cases occur since molecules can aggregate in one-dimensional or in two- or three-dimensional formations with valency links (molecular, fibre, layer or co-ordination lattices).



# ATOMIC DISTANCES IN ORGANIC COMPOUNDS BY X-RAY ANALYSIS

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**ABSTRACT.** Tables are given for the distances between the atoms or groups in diamond, graphite and a number of organic compounds. In the case of more complex structures, the results are classified according as the values were determined from Fourier projections in three independent directions, or by some less complete analysis.

IN the following tables an attempt has been made to classify the X-ray data on atomic distances in organic compounds according to the intensiveness of the analyses from which they are derived. Generally it is only in the case of the elements themselves (Table I) that the structures are sufficiently simple for the interatomic distances to be derived directly from the lattice constants of the crystal; then, of course, the

Table 1. Elementary structures

	Interatomic distances (Å.)		
Diamond*	C—C	1.541	
Graphite†	C—C	1.42	C...C between layers 3.41

\* W. H. Bragg and W. L. Bragg, *Proc. R. S. A*, **89**, 277 (1913). W. Ehrenberg, *Z. f. Kristall.* **63**, 320 (1926).

† J. D. Bernal, *Proc. R. S. A*, **106**, 749 (1924).

determination of distance is equivalent to the determination of wave length with the crystal as a grating.

In all ordinary organic compounds the asymmetric crystal unit is a group of atoms comprising part of the molecule, the whole molecule, or, in a few cases, several molecules. The precise position of each atom, and hence its distance from its neighbour, can then only be determined by the simultaneous evaluation of a number of parameters. The task usually appears rather hopeless in the case of complex structures, and probably would be were it not for the very extensive knowledge of the relative position and arrangement of atoms contained in the structural formulae of organic chemistry. These provide a framework and it remains to make this framework metrical and to deduce its orientation in the crystal. But in a complex structure it is practically impossible to disentangle the effects upon the calculated values of the intensities due to varying certain interatomic distances or to altering slightly the orientation of the model with respect to the crystal axes. When the work reaches this stage, the method of Fourier analysis is invaluable, because it presents a picture of

the structure which is built up from the experimental measurements, only the phase constants of the terms being taken from a preliminary trial and error analysis. This means that approximations to the structure differing slightly in orientation or in

Table 2. Layer structures and linear structures. Atoms all in one crystal plane, or dominantly along one crystal axis

	Interatomic distances (Å.)		Intermolecular distances (Å.) (minimum)	
Cyanuric triazide* (one Fourier projection)	C—N in ring	1·38	N...N	3·12
„	C—N outside ring	1·39		
„	N≡N terminal	1·11		
„	N=N	1·26		
Hexamethylbenzene† (Trial and Error Analysis)	C—C aromatic	1·42	CH <sub>2</sub> ...CH <sub>2</sub>	3·6–3·9
„	C—CH <sub>3</sub> aromatic-aliphatic	1·48		
n-Hydrocarbon‡, C <sub>29</sub> H <sub>60</sub>	CH <sub>2</sub> —CH <sub>2</sub> aliphatic	1·553§		
Hydrocarbon series‡	CH <sub>2</sub> —CH <sub>2</sub> aliphatic	1·534		

\* I. E. Knaggs. (Report in preparation.)

† K. Lonsdale, *Proc. R. S. A*, **123**, 494 (1929).

‡ A. Muller, *Proc. R. S. A*, **120**, 437 (1928).

§ Assuming tetrahedral angle.

Table 3. Complex structures. Analyses based on three separate Fourier projections

	Interatomic distances (Å.)		Intermolecular distances (Å.) (minimum)	
Anthracene*	C—C aromatic	1·41	CH...CH	3·7
Naphthalene†	C—C aromatic	1·41	CH...CH	3·6
Durene‡	C—C aromatic	1·41	CH <sub>3</sub> ...CH <sub>3</sub>	3·9
„	C—CH <sub>3</sub> aromatic-aliphatic	1·47		
Dibenzyl§	C—C aromatic	1·41	CH...CH	3·7
„	CH <sub>2</sub> —CH <sub>2</sub> aliphatic	1·58	CH <sub>2</sub> ...CH	4·1
„	C—CH <sub>2</sub> aromatic-aliphatic	1·47		
Benzoquinone	C—C in ring	~1·5	=O...=O	3·62
„	C=C in ring	~1·32	=O...CH	3·36
„	C=O	~1·14	C...CH	3·44

\* J. M. Robertson, *Proc. R. S. A*, **140**, 79 (1933).

† J. M. Robertson, *Proc. R. S. A*, **142**, 674 (1933).

‡ J. M. Robertson, *Proc. R. S. A*, **141**, 594 (1933); **142**, 659 (1933).

§ J. M. Robertson, *Proc. R. S. A*, **146**, 473 (1934); *Nature*, **134**, 381 (1934); (and report in preparation).

|| J. M. Robertson, *Nature*, **134**, 138 (1934); (and report in preparation).

atomic distances will all lead to the same final result, which has, therefore, the quality of a direct determination.

A double Fourier series is now generally employed, giving a projection of the structure in a certain direction. By piecing together the results of two or more pro-

jections of this kind, the whole structure can often be determined (Table 3). In the very rare cases in which all the atoms of the structure lie in one plane, a single projection perpendicular to this plane may sometimes give all the necessary information (Table 2). As the work is rather laborious, structures are sometimes satisfactorily determined by making a single Fourier projection and combining the

Table 4. Complex structures. Trial and error analysis combined with one Fourier projection

	Interatomic distances (Å.)		Intermolecular distances (Å.) (minimum)	
Chrysene*	C—C aromatic	1·41	CH...CH	3·4
<i>p</i> -Diphenylbenzene†	C—C aromatic	1·42	CH...CH	3·9
Hexachlorobenzene‡	C—C between rings	1·48		
Urea§¶	C—Cl	> 1·79	NH <sub>2</sub> ...=O	3·2
Thiourea	C—NH <sub>2</sub>	1·37	NH <sub>2</sub> ...NH <sub>2</sub>	3·8
„	C=O	1·25	NH <sub>2</sub> ...=S	3·4
„	C—NH <sub>2</sub>	1·35		
„	C=S	1·64		

\* J. Iball, *Proc. R. S. A.*, **146**, 140 (1934).

† L. W. Pickett, *Proc. R. S. A.*, **142**, 333 (1933).

‡ K. Lonsdale, *Proc. R. S. A.*, **133**, 536 (1931).

§ Wyckoff, *Z. f. Kristall.* **81**, 102 (1932); Hendricks, *J. Amer. Chem. Soc.* **50**, 2455 (1928).

¶ Wyckoff and Corey, *Z. f. Kristall.* **81**, 386 (1932).

|| Wyckoff and Corey, *Z. f. Kristall.* **89**, 462 (1934).

Table 5. Complex structures. Trial and error analysis only

	Interatomic distances (Å.)	
Hexamethylenetetramine (cubic)*	CH <sub>2</sub> —N	1·42
$\beta$ -Benzene hexabromide (cubic)†	CH—Br	1·94§
Diphenyl‡	C—C aromatic	1·42
„	C—C between rings	1·48

\* Dickinson and Raymond, *J. Amer. Chem. Soc.* **45**, 22 (1923).

† Dickinson and Bilicke, *J. Amer. Chem. Soc.* **50**, 764 (1928).

‡ Dhar, *Indian J. Phys.* **7**, 43 (1932).

§ Assuming tetrahedral cyclohexane ring.

|| Wyckoff and Corey, *Z. f. Kristall.* **89**, 462 (1934).

measurements obtained with previous knowledge of the true interatomic distances, in order to calculate the precise orientation of the molecules in the crystal (Table 4).

Interatomic distance is, of course, only one aspect of the results of a complete structure determination. Precise information can be obtained about stereochemical matters as valency angles, and the position taken up in the crystal by certain groups where free rotation is possible about a single bond. Some examples are shown in the following diagrams.

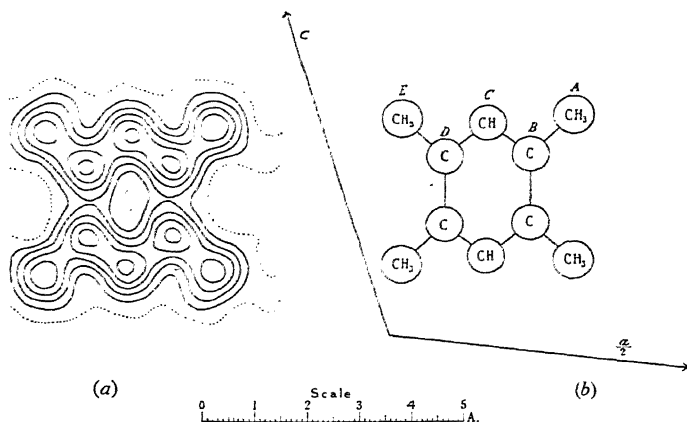


Figure 1. Durene (tetramethyl benzene) projected along the  $b$  axis. (a) shows the distribution of electron density by Fourier analysis and (b) is a diagram of the relative positions of the atoms in the structure. Each contour line represents a density increment of one electron per square Å. It is found that the methyl groups are displaced away from each other by about  $3^\circ$  beyond the symmetrical position. The plane of the ring is, of course, inclined to the line of projection, thus distorting it from a regular hexagon.

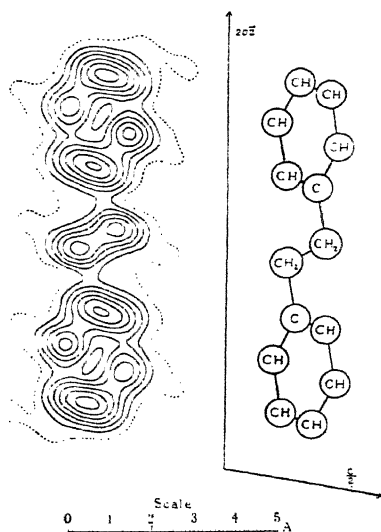
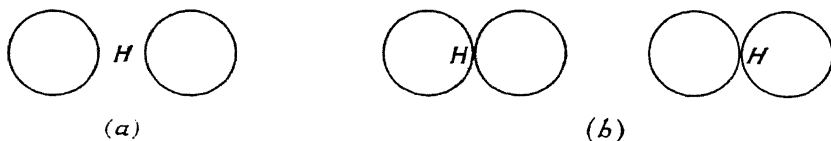


Figure 2. Dibenzyl projected along the  $b$  axis. It is found that the planes of the benzene rings are at right angles to the plane containing the zig-zag of the connecting CH<sub>2</sub> groups. The complete structure determination requires other projections at right angles to this one.

## DISCUSSION

J. D. BERNAL. The study of the nature of the interatomic bond in the solid state can be approached in a different way, viz. by studying the transitions from ionic binding to homopolar linking on the one hand and to van der Waals forces on the other.

A most interesting case is that of bonds involving hydrogen. The simplest of these is the acid hydrogen bond found in solid and liquid acids and acid salts and even in gases, as in such bimolecular aggregates as  $(\text{HCOOH})_2$ . In this bond as studied by Huggins and Pauling, the  $\text{H}^+$  ion may either be regarded as an ion with two oxygen (or fluorine) ions co-ordinated with it as in the left-hand figure,



or as a degenerate system resonating between the states shown on the right. In any case there is a very definite binding energy as is shown by the reduction of the effective radius of the oxygen atom to 1.27 Å. as against 1.34 for the  $\text{O}^{--}$  ion and 1.8 for the neutral Ne atom.

I have recently been studying, together with Miss Megaw, another type of bond—that occurring in alkali and amphoteric hydroxides, which may be called the hydroxyl bond. The analysis of the crystal structures of the main groups of hydroxides (with the important exceptions of those of Na and K) has enabled us to follow the changes that the hydroxyl group undergoes in different ionic environments. The determining factor appears to be the electric field to which the hydroxyl ion is subjected, determined by the size and charge of the metallic cation, i.e., in Goldschmidt's terms, by its polarizing power. The extremes are the low fields of the weakly polarizing alkali ions where the ion behaves essentially like a fluorine ion, and the high fields and strong polarizing power of  $\text{B}^{3+}$  or  $\text{Te}^{6+}$  where the binding of the cation to oxygen approximates to the homopolar force of the oxyacids, while the hydrogen becomes correspondingly loosely bound.

The nature of the change can be followed quantitatively by the measurement of the distance between the hydroxyl groups attached to different cations. The values are given below:

Cation	Li'	Ca''	Mg''	Mn''	Fe''	Zn''	Al'''	Te <sup>6+</sup>	B'''
Half distance between OH groups	1.80	1.88	1.61	1.56	1.53	1.41	1.39	1.38	1.35

There is an approximately linear relation between the logarithm of the interatomic distance and the energy of the cation hydroxyl bond. If we attempt to form a theoretical picture in wave mechanical terms it appears as a successive loss of degeneracy of the hydroxyl group with increasing fields. Free hydroxyl must have cylindrically symmetrical eigenfunctions. This is also probably its condition in the alkali hydroxides. With higher fields the tendency will be for the eigenfunctions to

split up into a tetrahedral configuration of a general methane-like character, though here only one of the concentrations of negative electricity will be occupied by a hydrogen ion. In the case of the intermediate bivalent hydroxides the three negative concentrations will be opposite the three cations, so that there is no essential difference from the case of a cylindrical group. In aluminium hydroxide only two of the negative concentrations are occupied by  $\text{Al}^{3+}$  ions and the remaining concentration can link with a hydrogen atom contained in a neighbouring hydroxyl group. This is the true hydroxyl bond, and it is significant that it gives the same interatomic distance 2.76 Å. as that found in ice and water. With boron, sulphur and tellurium hydroxides it is not certain whether one or two negative concentrations are attached to a cation, as here the binding must be essentially homopolar, but in any case one negative place is left for the reception of the  $\text{H}^+$  of a neighbouring hydroxyl group. The case of the neutral hydroxyl of the alcohols which exhibits marked hydroxylic binding must lie between these weak acids and the amphoteric hydroxides.

The relative weakness of the hydroxyl bond compared to the H bond is due to the presence of another  $\text{H}^+$  in the neighbouring OH group.

This semi-classical picture has served to interpret and even to predict quantitatively the crystal structure and properties of hydroxides, and it would be very interesting to see if it could be given a stricter quantum theoretical basis.

Prof. P. P. EWALD. Most measurements give a test of the wave-mechanical theory of molecules or of crystals by checking the energy values rather than the actual  $\psi$ -functions or the electronic distributions. There is, however, one case in which a test of the latter presents itself: in the case of diamond. The diamond structure was established by Sir William Bragg in 1913 chiefly by help of the missing second order octahedral reflection (222). Later, this reflection, though very faint, was found to exist. It is a direct evidence for a difference of orientation of the carbon atoms forming the two interpenetrating face-centred lattices, of which the diamond lattice is composed. Or, to put it in another way, this reflection shows that the carbon atoms cannot be spherical or contain a centre of symmetry.

Dr Hönl and I have been trying to apply to the case of diamond the methods used by Slater and Pauling for calculating directed valency bonds. We start with a tetrahedral ground state of the carbon atom which consists of a combination of one  $2s$  and three  $2p$  electrons. We have, so far, neglected all but the 4 nearest neighbours and have not gone beyond the zero order approximation. Where the eigenfunctions of neighbouring atoms overlap, an induced probability for the presence of electrons appears. Integration of the total amount of charge thus accumulated round the centre of the lines joining the nearest carbon atoms gives about 0.8 electrons round each centre. The L shell of each carbon is consequently weakened to contain  $4 - 4 \times \frac{1}{2} \times 0.8 = 2.4$  electrons only. It is possible, in an approximate way, to determine the Fourier expressions for the electron density in the unit cell of diamond. This gives the following Fourier coefficients (preliminary values!):

Order	(111)	(220)	(222)	(400)	(444)	(622)
Coefficient $ A $	15.6	19.6	0.24	12.7	9.6	$\sim 3.5 \cdot 10^{-7}$

The intensities to be observed by X-rays may be taken as proportional to  $|A|$  and would thus lead to the ratio  $(111) : (222) \sim 100 : 1.6$ , whereas the measurements of Sir William Bragg (after taking account of the angular functions) lead to  $(111) : (222) \sim 100 : 4$ .

It is thus highly probable that the  $(222)$ -reflection of diamond can be accounted for quantitatively by the tetrahedral deformation of the C-atoms and that an accurate Fourier determination of the lattice will show further details of this most important case of an unspherical atom.

Dr A. MÜLLER. The problem of cohesion in organic solids resolves itself quite naturally into two parts. The first is the formation of the molecule from its constituent atoms. The paper by Heitler and London on the homopolar bond in the hydrogen molecule marks a fresh stage in the development of theoretical chemistry.

The second part of the cohesion problem deals with the interaction between the whole molecules in an organic crystal. Here the theory of Eisenschitz and London on the van der Waals forces has opened up new possibilities for the interpretation of crystal properties.

In a subsequent paper London has made a particularly interesting application of this theory. He calculates the heat of sublimation of a number of crystals from optical data of the constituent atoms and the lattice dimensions of the crystals. One of the crystals is solid methane.

In this paper London confines himself to molecules which in the simplified calculation are to be regarded as points.

Considering the extreme importance of the cohesion problem it seems most desirable to extend these calculations to crystals the constituent molecules of which cannot be treated as points. The theory in its general form is not restricted to point-like molecules. The correct application to an extended molecule is practically out of the question; an approximate calculation, however, can be made under certain conditions.

I have made such an attempt and have calculated the van der Waals potential of a paraffin crystal. These calculations are tedious and the paraffin crystal was chosen for its obviously simple structure. The calculated values for the potential are found to be larger than the observed heat of sublimation. This is to be expected, for it must be remembered that the potential due to the repulsion forces has to be subtracted from the van der Waals potential.

The van der Waals potential is found to be 2.4 kg. cal. per  $\text{CH}_2$  gm. mol. if the  $\text{CH}_2$  groups are taken as points lying along the chain axes, and 3.7 kg. cal. per  $\text{CH}_2$  if the potential is calculated taking the nuclei of the C and H atoms separately in their correct position in the lattice. A calculation in which the centres are in the middle of the bonds gives an intermediate figure. The potentials are calculated for the crystal at room temperature. The observed value of the heat of sublimation is 2.1 kg. cal. per  $\text{CH}_2$  gm. mol. How much the calculated values will be reduced by the repulsive potential cannot be stated; it is not to be expected that it will make much

difference. The calculations can be regarded as confirming the theory within the limits which may reasonably be expected in this approximate treatment.

Prof. J. C. SLATER. Professors Hückel and Hund have pointed out the two methods which have been used for computing interatomic forces, the first depending on electron pairs, the second on molecular orbitals, and have indicated that the second gives results in better agreement with experiment. I wish to state that I am in entire agreement with this conclusion, and that I believe that the second method, in the approximation to which it can be conveniently carried, is better than the first in a corresponding approximation. As a matter of fact, most of the calculations made by the Heitler and London method of electron pairs have neglected so many terms, in the nature of interaction integrals between three or more wave functions, lack of orthogonality, etc., which we know by the work of Coolidge on the water molecule to be large, that they possess practically no theoretical significance. The calculations of Pauling, for instance, seem to make quite unwarranted use of the theory. But the very fact that it is so difficult to include these missing terms is a strong practical argument against the Heitler and London method.

I believe, however, that the probable future development of the theory will not lie exactly along the lines of either of these methods so far discussed. In a study of metals, the theory of which in some ways has advanced farther than that of other solids, it seems most convenient not to consider exchange or interaction integrals of the conventional type at all, and I believe these will become of less importance in the theory. Instead\*, it seems more convenient to consider separately the total potential and kinetic energies of the crystal, in their dependence on the positions of the atoms, relating them by the virial theorem. For the potential energy, we do not need to know the complete eigenfunction for all electrons of the crystal, but merely, as one can see from the work of Fock, a two-electron probability function, giving the probability that simultaneously electron number one will be at one point of space with one spin, and that electron number two will be at a second point with a second spin. The two-electron function is required because the potential energy involves only terms depending on pairs of electrons. Similarly the kinetic energy demands a one-electron probability in momentum space. The two-electron probability just mentioned involves the correlation between the positions of electrons with the same or opposite spins, as resulting from the exclusion principle, and it is this in particular which the method of electron pairs was designed to give correctly. But it now appears possible to determine this density approximately, following a suggestion of Wigner and Seitz, from the method of molecular orbitals. It has in this way been possible for metals, and one may hope that it will be possible for other solids, to give a tolerably complete account of the energy relations, by a method much more closely related to that of molecular orbitals than that of electron pairs, and much easier to understand in a physical way than the previous theories.

\* See J. C. Slater, *Rev. Mod. Phys.* (October, 1934).





# THE DEVIATIONS OF REAL CRYSTALS FROM THE IDEAL LATTICE STRUCTURE



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## THE MOSAIC TEXTURE OF ROCK SALT

BY P. P. EWALD AND M. RENNINGER

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**ABSTRACT.** An account of experimental work on crystals of rock salt, from which it is concluded that the mosaic texture is a property of individual crystals, and is not of necessity shared by all crystals of a given substance. X-ray examination showed differences, particularly in the integral reflecting power, between natural crystals, cleaved but untreated, and those prepared by the method of Kyropoulos, showing that the artificial crystal has no mosaic structure. Small areas were found agreeing with the perfect crystal in integrated reflection and in half-width.

Polishing of the surface of crystals from either source results in a value for the reflecting power characteristic of a mosaic texture.

Rock salt is stated in the literature to be a typical representative of the mosaic class of crystals—an assertion which presupposes that the mosaic character is invariably determined by the kind of crystal. An alternative to this is the hypothesis that the mosaic texture is not a general constitutional property but an individual one, i.e. that it is a property which results from the growth or deformation of individual crystal layers. This hypothesis must be the correct one, as is shown by the following measurements\*.

Rock salt, which had been taken without special precautions from the melt, in quantities of several c.c., according to the method of Kyropoulos, was tested by the "Divergence method" and gave an astonishingly sharp image of the reflecting surface, although, on examination by optical reflection, large areas of the surface were not absolutely perfect, but seemed broken up into strips which were several mm. wide and made angles of several minutes of arc with each other. ("Lineages" in Buerger's sense.) The reflecting properties of the surface were then investigated using  $\text{CuK}\alpha$  radiation for the  $(1\bar{1})$ -position in a double spectrometer. The reflection curve obtained for two extensive regions of a pair of cleavage surfaces extended over an angular range of about  $5^\circ$ . It consisted of irregularly distributed peaks, which were shown to correspond to the reflections from the individual disoriented crystallites.

In order to study the individual crystallites, an area of about  $1\frac{1}{2} \times 3$  mm. of the second crystal was singled out by means of thin lead foil, so as to give a good reflection image of the goniometer slit by reflection. The reflection curve on the double spectrometer was obtained by fixing the first crystal and rotating the second in steps of  $1^\circ$ . A bell-shaped curve resulted, having a half-width of  $7.1''$  (half-width at half maximum). This is near the predicted theoretical half-width for an ideally

\* For the full publication see M. Renninger, *Z. f. Kristall.* **89**, 344 (1934).

absorbing crystal, which would be  $5''$  according to the formula of Prins. The observed value of the half-width lies below all values of the half-width previously observed for rock salt by the double spectrometer, these being given as from  $30''$  to  $300''$ . By interposing a diaphragm with a hole of  $0.3$  mm. diameter it was possible to test different portions of the  $1\frac{1}{2} \times 3$  mm. area. In this way curves were obtained from different points, having sometimes secondary maxima which arise through reflections at adjoining areas or where there are inclusions. It may be that for the narrowest reflection curves of half-width  $7.1''$ , the difference from the theoretical value of  $5''$  is determined by a flat folding of a few seconds in the cleavage plane, extending also through the nearly ideal region. It is also possible, however, that the somewhat too great width results from the small extension of the reflecting crystallites, which limits the interaction of the rays postulated in the dynamical theory of interference.

If a larger area of the crystal (of  $30$ – $50$  mm<sup>2</sup>) is used, the reflection curves from the separate points consist of an irregular series of peaks which for the artificial crystals are some  $80$ – $100''$  apart, while for the natural crystal they may cover about  $1000''$ .

If the reflecting surface is polished, some degree of smoothing of the reflection curve occurs together with a noticeable broadening of the half-width to some  $1000''$  ( $15'$ ).

The *integrated reflecting power* proves to be independent of the presence of the diaphragm—as would be expected from the fact that each element of surface gives its appropriate contribution. Nevertheless from the integral reflecting power we can decide whether the reflection is mainly produced as the sum of contributions from ideal reflecting elements, or whether it approaches another limiting case, that of the pure mosaic crystal of Darwin. For the mosaic crystal has always the greater reflecting power, and moreover there exists a difference in the dependence on angle. By measuring the integrated reflecting power in different orders it is possible to obtain a verdict as to whether the reflected beam results from the dynamical interference effect of coherent regions extending over at least  $10^{-3}$  cm., or from the interference effect of mosaic crystals covering, at most,  $10^{-4}$  cm.

It appears now that undisturbed cleavage surfaces of artificial rock salt produce integrated reflection curves which agree with the curve for the ideal crystal as well as can be expected. The departures amount to  $+17$ ,  $+6$ ,  $-8$  per cent for the reflections (200), (400), (600), while the curve for the mosaic crystal is  $4$ – $5$  times the observed value. This clearly proves that the reflection at these undisturbed artificial rock salt crystals arises predominantly from the ideal regions, and that only unimportant disturbances arise out of the mosaic blocks.

It is explicitly emphasized that in this comparison with the theory of dynamic interference, use is made of

(1) The polarization factor  $(1 + |\cos 2\theta|)$ , instead of  $(1 + \cos^2 2\theta)$  for the mosaic crystal.

(2) The structure factor  $|F|$  instead of its square  $|F|^2$ .

(3) No separate determination of the effective absorption coefficient during reflection.

Moreover, the theoretical values are computed by means of

(a) Hartree's theoretical atomic factors, modified by a dispersion correction as given by Hönl on account of the relative closeness of the  $\text{CuK}\alpha$  radiation to the chlorine absorption edge.

(b) The usual absorption coefficients of Jönsson.

(c) The refractive index according to the Lorentz dispersion formula.

(d) The Waller-Prins formula for the interference effect in an absorbing crystal.

(e) The Debye-Waller temperature factor as determined by James, Firth and Waller for rock salt.

The experimental values were reduced by

( $\alpha$ ) Consideration of the polarization of the radiation incident on the second crystal due to reflection at the first crystal, and

( $\beta$ ) A correction on account of a small admixture of  $L$  radiation from tungsten, which was present in the primary beam, since this is reflected from the first crystal but not from the second.

Thus the dynamical theory in its best form at present has been used, and in it no values have had to be adjusted to fit the measurements.

In contrast to a freshly cleaved surface, the polished surface of the same artificial crystal gives an integrated reflection which agrees excellently with the curve for the mosaic crystal. The same values are obtained for a polished surface of natural rock salt. The values are some 4-5 times greater than the value given by an unpolished artificial cleavage specimen; they depart by less than 10 per cent from the values which are obtained from the usual formula for the mosaic crystal, when the secondary extinction is taken to have the same numerical value  $g = 320$ , as that given by Bragg, James and Bosanquet. We notice the fundamental difference which results from the polishing. Since the penetration of  $\text{Cu}$  radiation into  $\text{NaCl}$  is of the order of  $\frac{1}{10}$  mm., the crystallites must be deformed, broken up and transformed into a mosaic right into the interior. Here there is still parallelism within about  $\frac{1}{2}^\circ$  to the final surfaces, as may be seen from the breadth of the reflection curve ( $\pm 1000''$ ).

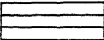



A natural rock salt crystal from the Kochendorf mine on the Neckar, which when cleaved had an optically rather warped surface, was tested without being previously polished, using the good artificial crystal as a monochromator. Although the whole reflection-curve from a large area extended over a large angle, yet by using the diaphragm of 0.3 mm. diameter, peaks of moderate width—about 30-50"—were obtained from the individual crystallites. The integrated reflection values were intermediate between those of the perfect and of the pure mosaic crystal. Evidently the coherent areas of the natural crystal are much smaller than those of the artificial, or else there are broad layers with mosaic texture between the coherent areas.

We have in this investigation realized both limiting cases, as well as the transition from one to the other in the same rock salt—which clearly contradicts the conception of the mosaic as being a constitutional property. Of course, we are dealing here with the "röntgen mosaic," i.e. a mosaic having particles of less than

$10^{-4}$  cm. For, in another order of magnitude, the optical ( $10^{-1}$  to  $10^{-3}$  cm.), the artificial crystal is also not homogeneous, but a mosaic of crystallites. It is shown by this investigation that the coarser and finer mosaics are not inseparably connected but that either can be present or absent without the other.

INFLUENCE OF CRYSTAL IMPERFECTION ON INTEGRATED INTENSITY OF X-RAY REFLEXION (Rocksalt (400) reflex with copper K-radiation)			
SIZE OF COHERENT DOMAINS / ANGULAR DISPLACEMENT	1 sec.	1 to $10^3$ sec.	Ord. of magnitude: degrees
$10^{-2}$ cm RAYS ABSORBED IN SINGLE DOMAIN	Reflexion as for perfect crystal		
$10^{-2}$ to $10^{-3}$ cm PARTIAL TRANSMISSION OF RAY THROUGH SINGLE DOMAIN			
$10^{-3}$ to $10^{-4}$ cm PRIMARY EXTINCTION REDUCED BY SMALLNESS OF DOMAINS			
$10^{-4}$ to $10^{-6.5}$ cm NO PRIMARY EXTINCTION LEFT.			
$<10^{-6.5}$ cm BROADENING OF REFLEX DUE TO SMALLNESS OF PARTICLES; NO SECONDARY EXTINCTION LEFT	Reflexion as for ideal mosaic crystal		

	Primary extinction effective		Integrated reflexion as for perfect crystal
	Secondary extinction effective		Integrated reflexion as for ideal mosaic crystal

There is another point we wish to make concerning the imperfections of crystals: it is of no use to speak, for example, of a mosaic structure in a general way. Our artificial crystal, though nearly perfect for X-ray reflections, was but a poor reflector for the beam from the goniometer and would not serve as a crystal for an X-ray spectrograph. In speaking of imperfections—as of every form of inhomogeneity—it is essential to state the scale applied, which varies according to the physical property considered.

From considerations of X-ray work it is thus possible to class the crystals into the table opposite, arranged first according to the *size* of coherent domains and secondly according to their *disorientation*.

It is evident from the table, for example, that for very small angular displacements the size of the coherent domains may vary much more than for larger domains, without deviations of the reflecting power from that of a perfect crystal, whereas the ideal mosaic reflection will be obtained with larger particles if only their angular sweep is large enough.

As is shown by the regions in which the primary or the secondary extinctions or the mass absorption are effective, it is even necessary to state the wave-length used: if, instead of copper rays, molybdenum rays had been used for the measurements, the divisions of particle size would have been different from those given. This shows how careful one must be in interpreting the results of measurements of crystal imperfections.

For working out an actual case, it has been necessary to state in the table the wave-length and the order of interference. By changing these the divisions will shift, especially where mass absorption is concerned. But the whole arrangement of the table will remain unaltered and may thus be regarded as giving general information on the type of crystal imperfection open to X-ray investigation.



## EXPERIMENTAL EVIDENCES OF GROUP PHENOMENA IN THE SOLID METALLIC STATE

BY ALEXANDER GOETZ

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*ABSTRACT.* The arguments in favour of some kind of superstructure in crystals are briefly mentioned, and it is explained that the word "group" is chosen to mean an agglomeration of a limited number of molecules in crystalline array, inside of which group the stability of a molecule is different from outside, and the size of which is a physical constant of the type of crystal under consideration. Thus a group structure neither accepts nor rejects the "secondary structure" dealt with by Zwicky.

The experimental evidence for the existence of groups is then reviewed.

Firstly, there is the evidence from etch figures on the cleavage planes of bismuth.

Secondly, there are phenomena at the transition from solid to liquid. Two observations here strengthen the case for a group structure, (a) the fact that the degree of super-cooling depends on the previous heating above the melting point, (b) the fact that the orientation of a crystal persists beyond the process of fusion, so that on subsequent solidification, the same orientation is found again. Again, the thermal e.m.f. of bismuth does not alter suddenly at the melting point, but changes gradually in a region of about 8° C. above the melting point.

Similar evidence is furnished by the behaviour of crystals formed partly within and partly without a magnetic field.

The third type of evidence is that from studying the distribution of the last traces of impurity. It would be expected that the foreign atoms would tend to segregate at the boundaries of the groups (a "surface" effect), and it is found in fact that there is a critical concentration where this changes to the more usual "volume" effect.

Finally, the comparison of the coefficient of expansion as measured macroscopically and by X-ray methods (which determine only the expansion inside the lattice, and ignore the boundaries) is discussed from the point of view of group phenomena.

It is the purpose of this paper to present a critical survey of experiments which can be interpreted as evidence of the existence of a higher periodicity in the crystal than the primary lattice structure. The discussion will be focused on experiments on metals, since the work of the author and his collaborators has been restricted to this field.

The need for an assumption of some kind of superstructure has originated from a large number of different fields of experience, e.g. the intensity of diffracted X-rays (Darwin), the anomalies of the tensile strength of crystals (Joffé, Smekal, Zwicky), phenomena of dissolving crystals (Traube and von Behren), etc. Accordingly, numerous theoretical attempts have been made to describe the nature of, and the reason for, the existence of such superstructures. As a consequence, the nomenclature is not uniform and, in order to avoid a confusion of terms, the word "group" has previously<sup>(1)</sup> been chosen by the author to designate an agglomeration of a

limited number of molecules in crystalline array, inside of which group the stability of a molecule is different from outside, and the size of which is a physical constant of the type of crystal under consideration. A "group phenomenon" is thus a quality of the crystal which can be described neither by assuming the crystal to present an infinite three-dimensional continuum nor by the assumption of more or less accidental discontinuities, as is represented for instance by the ordinary microscopically visible mosaic structure, characterized by measurable changes in orientation. On the other hand, the assumption that a crystal is an agglomeration of groups necessitates neither the acceptance nor the rejection of a "secondary structure" in the sense of Zwicky's theory.

This is not the place to discuss as a whole the different observations which make the assumption of a sub-division of a crystal necessary, especially since a number of very excellent treatises have been published recently<sup>(2, 3)\*</sup>.

Considerable difficulty is encountered if we seek for experiments giving more than circumstantial evidence for the existence of such groups in a real crystal. The question must first of all be settled: What constitutes a periodicity in a crystal with a good alignment of groups of approximately equal size? Here the physical nature of the group boundary becomes of great importance and we are forced to assume that the physical conditions for the atoms at the surface of a group are different from those of the atoms inside. This seems to be especially important in the case of foreign atoms, which will cause a greater reduction in stability inside the group than at the surface. Hence we shall find such impurities in very small concentrations in an adsorbed state at the group boundary, and the foreign atoms will establish sources

\* One trivial argument only may be pointed out which seems to speak rather definitely against the assumption of a crystal as a continuous repetition of the space lattice: the difficulty of producing large single crystals is a well-known experience; also, it is equally difficult, if not sometimes impossible, to prevent a substance from crystallizing in small crystals instead of remaining in an "amorphous" (i.e. non-crystalline) state. If the crystal were an ideal continuum, we should expect the minimum free energy of the  $N$  atoms available for crystallization to occur for a configuration in which they are all united in *one large perfect* crystal. The formation of a *large* number of *small* crystals would result in a larger free energy for the total system. In other words, the formation of *one large* crystal would be *more* probable than the formation of *many small ones*; at least it must be admitted, even if we make local fluctuations of conditions responsible for the occurrence of the large number of small crystals, that once a large crystal has been created, its disintegration into small crystals under external influences (gliding and twinning due to plastic deformation) should be a rare occurrence. Further, the reunion of the fragments into the large crystal by recrystallization should not only be possible but difficult to prevent. Experience shows, however, the opposite to be the case: first, it is sometimes exceedingly difficult to keep a large single crystal in this condition and prevent it from "aging" into mosaic conglomerates; second, once such disintegration has taken place, this process almost always proves irreversible under heat treatment. Since all this does not hold for crystals of small dimensions, we are led to assume that the above consideration is correct only for a limited value ( $\bar{N}$ ) of  $N$ . ( $N \leq \bar{N}$ ). In other words, if a crystal has reached a certain size containing  $\bar{N}$  atoms, the increase of stability of  $\Delta N = (N - \bar{N})$  added atoms is small or zero, so that a further growth is less likely and it can even be more probable that the  $\Delta N$  atoms (for a sufficient magnitude of  $\Delta N$ ) are more stable in the form of a new crystalline group which consequently reaches its maximum of stability after it in turn has grown to the content of  $\bar{N}$  other atoms. Thus a crystal would be true to its ideal definition only up to a certain size, and any real crystal of larger size would accordingly be a conglomerate of such elementary groups. It is easily seen that the stability of the whole system will not be influenced much by a slightly distorted arrangement of the conglomerate, which distortion will thus be probable. This argument, however, does not *necessitate* the presence of such distortions if, for instance, the conditions of growth are sufficiently well regulated and impurities absent, etc. The existence of large crystals with a high perfection in their goniometric relations is thus no fundamental argument against this concept.

of potential discontinuity throughout the crystal\*. The experimental evidence for the existence of such periodically repeated discontinuities would thus be obtained if it could be shown that the length of the period indicated by the distance of such potential walls was independent of the concentrations of the foreign atoms within certain limits. Such a finding would also prove that this type of precipitation of the foreign component is fundamentally different from the well-known accumulation of impurities (segregation) in certain regions of the crystal at high concentrations<sup>(4)</sup>. It may be mentioned here that we believe we have found experimental evidence for the invariance of the length of the period when the concentration changes about tenfold.

To render these discontinuities visible and accessible to measurement, the author initially used the chemical method, etching cleavage planes of bismuth crystals and observing the size and the formation of the etch pits under the microscope, correlating it at the same time with an equidistant line-pattern constructed by means of an Abbé mirror<sup>(5)</sup>. In addition, a system of equidistant lines indicating the threefold symmetry on the (111) plane of such crystals, was observed before etching took place.

The validity of the interpretation of these experiments as proving the existence of a higher periodicity in the crystal has met with various criticisms, e.g.<sup>(6)</sup> culminating in the suggestion that the source of the lines on the unetched plane represented some kind of plastic deformation affected by cleavage, and that the uniformity in the size of the etched figures was not sufficient to justify the assumption of a definite elementary unit (primitive perfect etch pit). These objections can be met in the following way: although the regions in which the line structures on the cleavage planes occur are the ones that look most perfect, and inspection of these regions under reflected polarized light does not give any indication of twin lamellae or other crystallographic discontinuities in the usual sense, no definite statement about the nature of such lines can be made owing to lack of means for investigating it. Their nature seems, however, to be of secondary importance to their occurrence at periodic intervals and the fact that the length of the period was found to be independent of the individual crystal. It has also been claimed<sup>(6)</sup> that the observed regularity was not a "real" but a "pseudo" regularity, especially in view of the fairly large margin of error of the microscopic observation caused by the closeness to the optical resolving limit. Against this the following general argument may be advanced: such a distinction presupposes a distinction between regularity and pseudo-regularity and does not seem to be justified. Considering the normal conditions of growth of a crystal, and the magnitude of the groups concerned, we should expect fluctuations in size which would render a perfect regularity impossible. In other words, the existence of a regularity *per se* seems to be established as long as a sufficiently large number of observations have been taken and a statistical distribution crowding around *one* value is found; the broadness of the distribution only

\* At this point it may be mentioned that it would be misleading to ascribe the existence of such structure only to the accident of the presence of impurities. This would seemingly be the same as ascribing the inner structure of an organic cell to the presence of a dye. Furthermore most crystals with which we have to deal are grown under such conditions that the complete absence of foreign atoms cannot be realized, and there is evidence that, even if the substance is of extreme high chemical purity, adsorbed gases may furnish the disturbing atoms.

renders the absolute value of the length of a period more or less uncertain, but does not affect the validity of the assumption that a periodicity exists. It thus seems that the situation is vastly different as between a Gaussian distribution, however broad, and a complete randomness: in the former case *we can evaluate finally a definite physical constant* characterizing the crystal (not the individual crystal) under consideration and we have to find a mechanism of crystal formation which can account for the occurrence and magnitude of this constant; in the latter case, the whole phenomena are attributed to mere accident. Thus, arguing along these lines it seems unjustified to establish a difference in principle between perfect and pseudo-regularity.

It is to be expected that the existence of groups would result in a great number of phenomena which should be accessible to experiment, in addition to visual observation under the microscope, this being at the same time the most direct method, and also the one most open to criticism.

As far as metals are concerned, the further (experimental) evidence so far available divides itself into observations at the transition from the liquid into the solid state and *vice versa*, and into certain properties of the crystal in the solid state. The subject will be treated accordingly in this order.

Concerning the transition from one phase into the other, there exist two seemingly important phenomena which yield evidence against the general assumption that a crystal loses its structure on passing through the melting point and, in our opinion, in favour of the hypothesis that the formation of groups antecedes the formation of the solid crystal: one is the observation of the dependence of the degree of supercooling upon the previous heating of the melt above the melting point, the other the persistence of the orientation of a crystal beyond the process of fusion.

Webster<sup>(7)</sup> has shown that for bismuth, lead and tin, the liability of the melt to supercool is larger, the more the melt has been superheated (heated above the melting point) previously. As far as metals are concerned, the observed differences were unusually large: it was possible to supercool bismuth to 40° by superheating the melt 80°, whereas superheating for only a few degrees permitted but a few degrees supercooling\*. It is obvious that the dependence of the degree of supercooling upon the thermal history cannot be reconciled with the idea that the crystal builds itself from single individual molecules out of the melt, since the kinetics of the molecules in the liquid and their interaction cannot depend on the degree to which the liquid had been heated previously.

With regard to the process of melting, the author has first observed in bismuth crystals<sup>(8)</sup> that the orientation as well as the microscopic properties of the individual crystal (regions of different orientation, twin lamellae) are preserved in the melt for several degrees above the melting point, as is indicated by their reappearance if the melt is kept from mechanical disturbance and recrystallized into a single crystal. These observations on "latent" crystals have recently been confirmed independently<sup>(9)</sup>. The fact that the capacity of a molten single crystal for accepting an orientation different from its previous one on inoculation with a new seed crystal

\* The author found recently that pure gallium shares this property to a remarkable extent.

depends on the degree to which it was previously superheated, points in the same direction. Similar phenomena are well known to occur for liquid crystalline substances at the transition from the solid into the smectic state<sup>(10)</sup>.

Very little material is available concerning the degree of abruptness with which the physical qualities of a crystal, characteristic of its solid state, disappear when fusion sets in. The nature of the phenomena to be expected is such that one would think them most likely to be overlooked if no special care were taken to keep the crystal "latent". Only the experiments of Soroos<sup>(11)</sup>, concerning the disappearance of the thermo-electric e.m.f. of bismuth crystals, strengthen the assumption that the configuration which causes this property to be different from that for the liquid state survives the fusion to a certain extent for several degrees. He found that the e.m.f. characteristic of the solid crystal does not change discontinuously into the e.m.f. of the liquid but that this transition is gradual and is spread over a temperature range up to 8° above the melting point.

Into the same group fall experiments which deal with the possibility of changing the physical properties of an anisotropic metal by studying its crystallization in a magnetic field. It has been known for a long time that under such circumstances these crystals show an orientation in which the most paramagnetic direction of the crystal is oriented parallel to the lines of force of the magnetic field<sup>(12, 13)</sup>. In recent years we<sup>(14, 15)</sup> have tried to study such phenomena under more controlled conditions, and it was found that it is actually possible to obtain single crystals with different properties (thermal e.m.f., electric conductivity, density) if one half of the crystal is grown within, and the other outside the magnetic field, although the external appearance does not show any crystallographic difference between the two halves. Also this indicates that the crystal must have existed before it became rigid, since a directional effect upon the crystal can only be impressed upon it by a magnetic field if an anisotropy exists which cannot be present in a liquid in which all the molecules are free to move independently of each other. The objection<sup>(16)</sup> that the difference can be ascribed to some kind of plastic deformation caused by the ponderomotive forces of the magnetic field can be met, however, by the argument that the absolute values of the susceptibility are so small that, within the range of fields used, the forces must remain far below the elastic limit of the crystal near the melting point. Thus it only seems possible to assume a plastic deformation of the liquid, i.e., of the groups before they reach the rigid state. Again, we have here a direct analogy with the behaviour of paracrystalline liquids, where it has been shown<sup>(17)</sup> that the alignment of the molecular swarms can be influenced in a similar way by a magnetic field.

The chief experimental evidence against the existence of such groups in the immediate neighbourhood of the melting point was the fact that it was impossible to obtain X-ray patterns which indicated more regularity than the usual statistical arrangement of molecules. The following arguments, though, can be brought against the validity of such evidence: it is known that the geometric arrangement of most metals in the solid state is that of a statistical—close packed—agglomeration of atoms, which varies in general only very little from the ideal configuration of packing for spherical molecules. We should thus not expect to find a large change even if the

atoms were agglomerated in some form of paracrystalline configuration. An exception of course is formed by metals which in their solid state differ largely from the statistical arrangement, such as bismuth, arsenic, antimony, gallium, tin, indium, etc., and it has actually been found for tin and gallium that close to the melting point, the intensity distribution for the molten metal differs from that indicating the simple statistical distribution. In the case of gallium the periodicity was found to fit even better with the structure of the solid state<sup>(18, 19)\*</sup>. Unfortunately there is no experimental material available yet for molten anisotropic metals close to the melting point, except those mentioned.

Summarizing this set of phenomena, it can be said that they necessitate the assumption of a persistence of the crystalline structure beyond the fusion of the crystal, which in turn necessitates the assumption that a crystal cannot be formed without the preceding formation of such paracrystalline agglomerations. However, the material is exceedingly scarce and the evidence can certainly not yet be called conclusive.

On account of the greater accessibility and the seemingly more general interest, our efforts have mostly been directed towards tracing group phenomena in the solid state. As has been discussed at the beginning of this paper, the effect of the last traces of impurities in small concentrations proves to be of assistance, in a similar way to the dye in biological microscopy. Two conditions have to be fulfilled, viz. the impurity must be soluble within the range of concentration used, and the concentration must be so small that a volume effect is not noticeable (i.e. 1 : 100 to 1 : 40,000). As indications for the effect of foreign atoms in bismuth crystals, we chose the magnetic susceptibility, the conductivity and the thermoelectric e.m.f. Several hundred crystals were grown and several thousand observations were taken of the susceptibility in different directions in the crystal in the range from liquid air temperature to the melting point, as a function of the concentration of the impurity and of its relative difference in the electron configuration to the bismuth atom<sup>(20)</sup>. From the standpoint of group phenomena, the interesting result is that we find a *critical concentration* of the admixture, below which the specific effect of the foreign atom is from ten to one hundred times larger (depending on temperature and type of impurity) than above. This apparently has to be interpreted as an indication that below the critical concentration we are dealing with a surface effect, whereas for higher concentrations the usual volume effect sets in. The authors have thus suggested that the foreign atom is absorbed at the internal surface of the crystal and that the critical concentration is reached when the internal surface is saturated, i.e. when, according to the picture outlined above, the group boundary is populated by foreigners to such an extent that the loss of stability caused by a further insertion of foreigners into the boundary equals or exceeds that due to absorption into the volume of the group. According to expectation, the critical concentration is exceedingly well defined at low temperatures, and its value proves to be reproducible and independent of the conditions of growth of the crystal within the available variations. The values for the critical concentrations were found to be: ca. 0.09 per cent atoms

\* The author found recently that pure gallium shares this property to a remarkable extent.

for tellurium, 0.3 per cent for tin, 0.9 per cent for lead and selenium. It is seen that these concentrations are not only far below the limit of volume solubility as indicated in the phase diagram, but also that there exists a proportionality between the critical concentration of an element and its saturation in the crystal, e.g. the phase diagram indicates that the solubility of tin in bismuth is approximately one-third of that of lead in bismuth (1.7 and 5.3 per cent) and the same ratio prevails between the respective critical concentrations. Since the volume solubility of a foreign atom in a crystal can be taken as a measure of the increase of total free energy of the crystal on the insertion of the foreign component, a similar respective increase will be effected by the adsorption at the group boundary; thus, for instance, one tin atom will cause as much disturbance in the boundary as three lead atoms, and consequently the critical concentration of tin will be one-third that of lead. If the group boundary is thus saturated, the effect upon the crystal is perfectly definite and there is no possibility of deciding from the physical properties of the crystal whether it contains tin as foreign admixture or lead in three times the concentration. The existence of such a critical concentration points definitely towards the existence of groups of approximately equal size, especially since the volume of the groups calculated under the assumption of a monomolecular population of the group boundary by foreigners at the critical concentration, proves to be of the same order of magnitude as the one calculated from the above mentioned experiments on primary etch pits. It amounts to  $10^{-14}$  to  $10^{-15}$  cm<sup>3</sup>. The complexity of these phenomena is greatly increased by the fact that foreigners such as tin, which are left-hand neighbours to the crystal atom (bismuth) in the periodic system, affect the crystal in a crystallographic direction opposite to the right-hand neighbours, e.g. tellurium to bismuth. For such details reference must be made to the original publication<sup>(20)</sup>. Measurements on the localization of traces of polonium dissolved in bismuth crystals<sup>(21)</sup> support this point of view inasmuch as a distinct statistical crowding around a definite distance ( $0.54\mu$ ) between the loci of high polonium concentration along [111] was found which is in excellent agreement with the distance of the (111) layers measured microscopically.

If the group boundary is the locus for a disturbance of the continuity of the space lattice, we should expect it to affect the thermal dilatation of a crystal in a way which is accessible to experiment. It is known that the thermal dilatation is definitely a co-operative phenomenon, i.e. that to produce a large thermal expansion it is necessary to have a large number of atoms in good geometric configuration, whereas a disturbance of this array will cut down the expansion accordingly. We should therefore expect that the region across the group boundary would not contribute to the thermal expansion of the whole crystal, especially at higher temperatures in the presence of impurities, since here the region of disturbance will penetrate far into the individual group. If we thus compare the thermal dilatation measured with a sensitive dilatometer over the whole length of the crystal, with the increase of the lattice parameter, the temperature coefficients should be systematically different, since the disturbed regions are not recorded by the X-rays, whereas the dilatometer integrates over the crystal as a whole. Thus the lattice expansion should come out to be larger than the integral expansion. The first measurements of this

kind were performed in our laboratory<sup>(22, 23)</sup> on bismuth crystals containing 0.1 per cent impurities and a very large divergence was found between the two kinds of dilatation; later, Jay<sup>(24)</sup> determined the thermal expansion by the powder method on very pure material and came to the conclusion that this divergence was very small if it existed at all. In continuation of the original experiment our previous results were checked during the last few years with more refined methods, especially with regard to the integral expansion, and the exact quantitative analysis of the content of foreign atoms in the crystal<sup>(25, 26)</sup>. A partial agreement with Jay's results could be obtained inasmuch as it was found that for very pure material (99.998 per cent or better) the divergence mentioned disappears for high temperatures owing to a change of the macroscopic (integral) expansion. This indicates clearly that the disturbance by impurities must take place in discrete regions of the crystal and not in the volume. The present experimental material seems to justify the assumption that it is *not* possible to affect the lattice expansion by the insertion of foreign atoms in concentrations of the order of the critical concentration. For the details also in this case, reference must be made to the original publications.

Another way of approaching the nature of group phenomena experimentally has already been indicated. If the stability of a crystal depends on its size, in the sense that a crystalline agglomerate of a small number of molecules ( $N \leq \bar{N}$ ) has a stability different from a crystalline agglomerate containing a larger number of molecules ( $N > \bar{N}$ ), we should expect certain types of physical properties of the crystal to become dependent on the size of the crystal as soon as its magnitude exceeds the critical magnitude ( $N = \bar{N}$ ). It is obvious that these types of property would be identical with those affected by the insertion of foreign atoms in the crystal, e.g. the crystal diamagnetism, conductivity, Peltier effect, integral expansion. On account of experimental difficulties, only the susceptibility has been investigated so far, and during the last three years, methods have been developed at our laboratories to render the measurement of such qualities accessible to experiment. The early work in this field performed in India<sup>(27, 28)</sup> has already given clear indication that the susceptibility of colloidal suspensions of graphite, bismuth and antimony becomes definitely dependent on size when the particle size becomes of the order of  $10^{-4}$  cm. One of the main sources of error in the exact determination of this size function lies in the anisotropic qualities, and the large error which results from measuring with a large number of particles which, owing to their non-spherical shape, arrange themselves according to a statistical law. We have avoided this difficulty by producing suspensions of crystalline particles in which the particles are all fixed in a crystallographically parallel position to each other, so that their physical properties can be measured in different directions with respect to their crystal orientation<sup>(29, 30, 31)</sup>. The principal difficulty in these experiments lies in the exact determination of the size function: if the dependence on size were caused by a surface effect (e.g. adsorption of paramagnetic  $O_2$  in case of a diamagnetic susceptibility of the crystal), the size function should follow a hyperbolic law, since the diamagnetism should then decrease inversely proportional to the diameter of the particle, whereas the existence of a critical size should be indicated under sufficiently controlled experimental



conditions by a curve which approaches a pronounced break when this magnitude is reached. The experiments of the Indian authors so far indicate a hyperbolic function, whereas our results on very carefully purified material and a small margin of particle size, point definitely towards a larger change in the size function in the critical region than can be described by an hyperbola. It could be proved especially that there is no dependence on size for particles above  $5 \times 10^{-4}$  cm. diameter.

A crucial experiment to decide between a mere accidental surface phenomenon and an innate property of the crystal is seen in the measurement of these properties at different temperatures, especially in the lower temperature region, since it is to be expected that surface adsorption would change the size function considerably with temperature, whereas the size of the group should obviously stay unaltered. Experiments of this kind are in progress but have not yet yielded definite results.

In conclusion, the picture derived from the group hypothesis may be recapitulated: Before entering the solid state in crystalline form, a metal has to go through a paracrystalline interphase in which molecular groups are formed, inside which the geometric configuration is already close to that of the solid lattice. The size of these groups is a physical constant of the crystal and lies between  $10^{-14}$  and  $10^{-15}$  cm<sup>3</sup>. The boundaries of these groups may give rise to discontinuities in the solid crystal. Furthermore, these boundaries form an internal surface of definite area in the large solid crystal, on which foreign atoms are adsorbed as long as their concentration is smaller than the concentration needed for saturating the surface. This concentration is called the critical one and is reflected in the concentration diagrams at low temperatures by a sharp decline of the specific influence of the foreign atom upon a number of physical qualities of the crystal. This critical concentration is a constant characteristic for any combination of totally or partially soluble metals.

Whereas it cannot be denied that the experimental support for this hypothesis is still very meagre and mostly of circumstantial nature, and that it is collected from metals generally considered to have unusual properties, it seems to us that already there exists sufficient material which does not lend itself to an interpretation along the traditional concepts of the formation and the constitution of a metallic crystal. The attempt to interpret this material by means of the above hypothesis is admittedly primitive and in many ways much less detailed than other attempts to describe discontinuities in non-metallic crystal lattices. It is also probable (even most likely) that a good deal of the elements of this hypothesis can be found in the theories of other authors. The justification of this exposition should thus be seen only in the attempt to point out a number of experimental results and to describe them as consistent with the picture to the composition of which a minimum of purely hypothetical material had to be used.

#### REFERENCES

- (1) A. GOETZ. *Z. f. Kristall. Sonderheft* (1934).
- (2) A. SMEKAL. *Handb. d. Phys.* 24, 2 (1933).
- (3) F. ZWICKY. *Rev. Mod. Phys.* 6, 193 (1934).
- (4) M. STRAUMANIS. *Z. f. anorg. Chem.* 180, 1 (1929).

- (5) A. GOETZ. *Proc. Nat. Acad.* **16**, 99 (1930).
- (6) M. J. BUERGER. *Z. f. Kristall.* Sonderheft (1934).
- (7) W. L. WEBSTER. *Proc. Roy. Soc. A*, **140**, 653 (1933).
- (8) A. GOETZ. *Phys. Rev.* **35**, 193 (1930).
- (9) E. DONAT and A. STIERSTADT. *Ann. d. Phys.* **17**, 897 (1933).
- (10) W. BRAGG. "Liquid Crystals." *Roy. Inst. Gr. Brit.* (Nov. 1933).
- (11) A. SOROOS. *Phys. Rev.* **41**, 516 (1932).
- (12) S. PLÜCKER. *Pogg. Ann.* **76**, 583 (1849).
- (13) M. A. LEDUC. *C. R.* **140**, 1022 (1905).
- (14) A. GOETZ and M. F. HASLER. *Phys. Rev.* **36**, 1752 (1930).
- (15) A. GOETZ and A. B. FOCKE. *Phys. Rev.* **37**, 1044 (1931).
- (16) H. E. BUCKLEY. *Z. f. Kristall.* Sonderheft (1934).
- (17) H. ZOCHER. *Rep. Far. Soc.* p. 945 (1933).
- (18) F. SAUERWALD and W. TESKE. *Z. f. anorg. Chem.* **210**, 247 (1933).
- (19) H. MENKE. *Phys. Z.* **33**, 393 (1932).
- (20) A. GOETZ and A. B. FOCKE. *Phys. Rev.* **45**, 170 (1934).
- (21) A. B. FOCKE. *Phys. Rev.* **45**, 219 (1934); **46**, 623 (1934).
- (22) A. GOETZ and R. C. HERGENROTHER. *Phys. Rev.* **40**, 643 (1932).
- (23) T. L. HO and A. GOETZ. *Phys. Rev.* **43**, 213 (1933).
- (24) A. H. JAY. *Proc. Roy. Soc. A*, **142**, 237 (1933).
- (25) J. W. BUCHTA and A. GOETZ. *Phys. Rev.* (In press 1934.)
- (26) R. B. JACOBS and A. GOETZ. *Phys. Rev.* **47**, 94 (1935).
- (27) V. J. VAIDYANATHAN. *Ind. J. Phys.* **5**, 559 (1930).
- (28) S. R. RAO. *Ind. J. Phys.* **6**, 241 (1931).
- (29) A. GOETZ, A. B. FOCKE and A. FAESSLER. *Phys. Rev.* **39**, 169, 553 (1932).
- (30) A. GOETZ and A. FAESSLER. *Phys. Rev.* **40**, 1053 (1932).
- (31) A. GOETZ. *Phys. Rev.* **45**, 282 (1934).

## ON THE CAUSE OF THE LOW VALUE OF MECHANICAL STRENGTH

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*ABSTRACT.* The discrepancy of the order of 500 times between the theoretical values of tensile strength and the values normally observed is recalled, and it is pointed out that amorphous substances show a similar discrepancy.

Two kinds of rupture are distinguished: (1) plastic rupture, in which there is a reduction of area at some point before fracture occurs; (2) brittle rupture.

The influence of plastic deformation on strength is then considered in some detail.

Brittleness occurs if the elastic limit increased either by previous plastic deformation or by lowering of temperature reaches the practical tensile strength. Two types of explanation have been put forward to account for this: (a) internal faults and (b) surface crevices.

Many experiments proving the importance of surface conditions are next described, among them that of dissolving the surface of rock-salt in hot water during the loading experiment; this raised the strength twenty times.

The conclusion reached is that the practical weakness is due essentially to the sharp discontinuities present on the surface.

### § 1. TENSILE STRENGTH AND MOLECULAR COHESION

TENSILE strength may be regarded as a measure of the molecular forces holding a material together. However, it is well known that the mechanical strength is usually many thousand times lower than would be expected from the theory of crystal lattices. This disagreement is easily explained by a closer examination of the mechanism of rupture. The local stress at the region where rupture takes place is always many times greater than the mean value over the whole cross-section. The best evidence that this is the case is provided by the splendid experiments of Griffith on the influence of discontinuities on the tensile strength of glass.

There are various reasons for assuming that the real molecular cohesion greatly exceeds the average stress during rupture.

(1) There is the disagreement that exists between theoretical and practical values (for rock-salt 200 kg./mm<sup>2</sup> and 0·4 kg./mm<sup>2</sup>), while the ordinary lattice theory gives quite consistent results for the energy of the crystal.

(2) Rupture is often observed in that stress region where Hooke's law still obtains, while any theory of molecular forces would predict that the maximum stress leading to rupture would be reached gradually. The modulus of elasticity as a derivative of stress upon strain must reach zero value at the maximum value of the force of cohesion.

(3) While tensile strength has a definite value as measured by the usual method, it may change many-fold if the test conditions are altered. Measured in hot water, the strength of rock-salt increases from 0.4 to 10 kg./mm<sup>2</sup> (Joffé, Levitskaya and others); protected from surface crevices, the strength of glass increases ten times (Griffith); mica stretched in such a way that the edges remain stressless, increases in strength from 30 to 300 kg./mm<sup>2</sup> (Orowan). In all these cases only the surface conditions were specially selected, while nothing was changed in the interior of the body; the average atomic distance as determined from the density gave the usual value.

The problem of practical weakness of materials is not confined to crystal lattices. Amorphous glass shows the same discrepancy of practical weakness and theoretical strength and the same large influence of surface conditions. We shall however consider crystals in the first place.

## § 2. PLASTIC RUPTURE

It will be useful to distinguish two kinds of rupture, plastic and brittle. The first type is usually manifested by a reduction of area on some cross-section where final fracture occurs. The second type occurs without appreciable plastic deformation. We may obtain both kinds of rupture on the same material by varying the rate of loading.

The general case is the rupture of a crystal which has previously been deformed plastically. The elastic limit of a single crystal is very low. Kirpitcheva, Levitskaya and myself first found, using X-ray methods, a value for rock-salt of 920 gm./mm<sup>2</sup> at room temperature, decreasing at the melting point (800° C.) to zero. At this stress of 920 gm./mm<sup>2</sup> we observed a change in the Laue diagram. Every spot (except one) became double; at higher loads it became divided into a series of spots changing the Laue diagram into a system of "tails" instead of single spots. We stated then, that this limit corresponded to a flow of the crystal and not to the first change in the lattice. Measurement by a mechanical device reduced the observed value of the "elastic limit" to 200 gm./mm<sup>2</sup>; an optical method developed by Obreimov (the appearance of double refraction along the gliding planes) gave a still lower value of 70 gm./mm<sup>2</sup>. By careful annealing of both pure artificial and natural crystals, Classen-Nekludova was able to observe the first fringe of double refraction at 9–10 gm./mm<sup>2</sup>. The same value has been found by Podashevski using the change of photoelectric current produced by plastic deformation.

The elastic limit of carefully prepared single metallic crystals is equally low. It increases rapidly as plastic deformation proceeds up to the point where continuous flow commences. Our opinion, that a high elastic limit for shearing stresses is characteristic of a solid body and distinguishes it from a liquid, is founded on the study of glasses, polycrystalline materials and crystals which have been previously plastically deformed. A crystal lattice, as such, is characterized by a very low elastic limit.

When plastic deformation precedes rupture, the mechanical properties of the

crystal are thereby changed. We shall consider what influence the phenomenon of plastic deformation has on strength.

In 1918, Kirpitchenova and myself\* showed that the plastic deformation of a rock-salt crystal leads to distortion of the crystal lattice along definite crystalline planes. By slipping and twinning on these planes, the crystal becomes divided into a large number of pieces, neighbouring pieces having relative orientations. Obreimov and Shubnikov†, using double refraction methods, have measured the stresses existing at the boundaries of the pieces and found tensile and compressive stresses, on opposite sides, of intensities up to 10 kg. mm<sup>2</sup>. The pieces are thus in equilibrium (Masing‡). Investigating carefully the mechanism of such plastic deformation, Classen-Nekudova§ found the phenomenon of deformation (first observed by P. Ehrenfest and myself), to consist of multiples of unit shearing motions, each consisting of a large number of such unit slips. A theory of this phenomenon has recently been given by Orowan.

Stepanov¶ suggested that the energy developed at a thin boundary layer during the short time occupied by a slip or "jump" ought, temporarily, to raise the temperature of the layer. He seems to have confirmed his assumption by the observation of a temporary increase of conductivity of rock-salt crystals along the gliding surface during a plastic deformation. If in other crystals the melting point was not reached, a considerable change of temperature manifested itself by the appearance of new high temperature manifestations such as annealing, recrystallisation, etc.

Thus plastic deformation possesses many features which tend to obscure the real strength which Stepanov assumes is developed at rupture.

(1) During the short period of slipping, the cohesion in the boundary layer involved is greatly reduced, possibly even to the value for the liquid state as given by the capillary constant. Discontinuities may be formed during this period, especially at higher temperatures near the melting point of the crystal.

(2) The sliding produces, inside the crystal and on its surface, discontinuities which may act as "crevices" and reduce the strength. This effect seems to be most important at average temperatures.

(3) Both layers adjacent to a boundary of a region of slip are left in a stretched or compressed state. Stresses much larger than the practical strength disappear at a rate which falls with decrease in temperature. They are added to the elastic stress produced by external forces and lead to a distortion of the crystal. Those stresses are especially dangerous at low temperatures.

Contrary to Stepanov's theory, we are accustomed to consider that plastic deformation increases tensile strength; but the influence is secondary. Plastic deformation increases the elastic limit mainly by a distortion of the regularity of the lattice. Up to a new enlarged limit no sliding occurs and therefore there is no chance for rupture. Increasing the amount of slip results in the production of

\* *Phil. Mag.* 43, 204 (1922).

† *Erg. Exakt. Naturwiss.* 2, 206 (1923).

.. *Z. f. Phys.* 89, 634 (1934).

† *Z. f. Phys.* 41, 907 (1927).

§ *Z. f. Phys.* 55, 555 (1929).

¶ *Sow. Phys.* 2, 26 (1932).

increasingly large stresses and discontinuities until at some point (most probably on the surface) the theoretical strength limit is reached. The development of such a discontinuity leads then to rupture.

Amorphous bodies such as resins, glasses and varnishes do not show any influence of plastic flow, either on the elastic limit or on mechanical strength.

### § 3. BRITTLE RUPTURE

If the elastic limit increased by previous plastic deformation (rock-salt) or by lowering of temperature (quartz) reaches the value of the practical tensile strength, the material becomes brittle. Rupture occurs either without any plastic deformation or at the first sliding; the observed strength is, however, much lower than the theoretical value. Two different explanations have been proposed to explain this discrepancy: internal faults (Smekal's "Lockerstellen" and Zwicky's "secondary structure") and surface crevices (Griffith, Joffé). There is no doubt that some kind of internal faults may act in just the same way as surface crevices (less dangerous, however, because the concentrated edge stresses may be lowered by plastic flow of the material and changed to a more uniform distribution). Sharp edges of a crystal included in a metallic body will probably also decrease mechanical strength. However, whether or not irregularities are produced by heat motion during crystallization, the frequently observed mosaic structure of a crystal would have the opposite effect. As such irregularities render gliding on a crystalline plane more difficult, they increase the elastic limit and therefore ought to increase the strength.

In the case of rock-salt, two experiments were performed by Levitskaya and myself to demonstrate the importance of surface conditions. Dissolving the surface by hot water during the loading experiment, we found strengths exceeding the usual value by a factor of twenty or even more. Many objections were raised against the conclusion drawn from our experiment. Polanyi ascribed both the high strength and the exceedingly marked plasticity to a lowering of the elastic limit by water. But no change in the elastic limit was found on careful measurement. Smekal in his first paper on this subject, and later Barnes, assumed that the penetration of water inside the crystal through narrow canals makes the gliding easier and leads to an increase in strength. (Experiments carried out under Smekal's direction changed his opinion.) This assumption however is in contrast with our observation that a saturated solution of salt has no influence at all, while it is clear that the water inside the rock-salt crystal must be saturated in any case. A direct disproof of the water penetration explanation was given by Classen-Nekludova. She protected a small strip of the crystal by vaseline. Notwithstanding the fact that practically the whole surface, except the small strip, was dissolved to a large degree in hot water and the penetration of water in the crystal could, and probably did, proceed just as easily as without the protecting strip, the strength observed was the strength of a dry crystal. Thus it was shown that the smallest dry spot on the surface may be responsible for the practical weakness of the whole crystal.

In our second experiment we used a sphere of rock-salt cooled carefully at liquid air temperature and then suddenly plunged into hot water or into molten tin. (Grünberg's calculations of the distribution of heat and stress show that after 1-2 seconds the central part must be stretched by the heated outside layer, while the outside surface is still unstressed.)

Neglecting the plastic stretching of heated sheets, we should expect a uniform tensile stress of about  $70 \text{ kg./mm}^2$  at the centre of the sphere. The plasticity of the warmer part will somewhat decrease this value, but it certainly exceeds the practical strength many times.

Still more conclusive are the experiments of Orowan on mica. Applying a tensile stress to the middle part of a plate of mica in such a way that the edges were practically unstressed, Orowan obtained values for tensile strength exceeding by ten times the strength obtained in the case where edges were involved. In a second experiment, Orowan observed that sheets of mica without crevices on the edges and giving a high strength, had a very low acoustical damping and emitted a clear sound. The same sheets with crevices on the edges gave a dull clang and had a low strength.

The influence of surface conditions was similarly found by Davidenkov and Wittmann on polycrystalline steel. Measured by a pendulum blow, they found a definite temperature (about  $-120^\circ \text{C.}$ ) where the brittle rupture changed to a plastic one. This transition point (which is the crossing point of the strength curve and the elastic limit curve as functions of temperature) decreased by  $20^\circ \text{C.}$  if the surface of the steel sample was polished or etched. It means that the tensile strength was increased by the removal of surface discontinuities.

The theory and well-known experiments of Griffith on glass also afford evidence of the influence of surface crevices on the tensile strength even for amorphous materials.

All the experiments described lead us to the conclusion that the practical weakness is principally due to sharp discontinuities mainly present on the surface and cannot be ascribed to small internal faults, "Lockerstellen" mosaic structure, or the like. In special cases only, there might exist an internal discontinuity of the same kind as a surface crevice.

Internal faults of a real crystal are however important for the mechanical behaviour as they increase the elastic limit and thus change the distribution of concentrated stresses responsible for the rupture at low temperatures. On the other hand, initial irregularities may lead by a plastic gliding to a sharp discontinuity on the surface, where the breakdown starts.

## ON THE MECHANISM OF BRITTLE RUPTURE

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*ABSTRACT.* A considerable amount of experimental evidence is collected together to show that the weakness in tension of substances such as glass and quartz is due to irregularities on the surface. Thus it is well known that the strength decreases with increasing thickness; it is now shown that dissolving away a layer from the surface of a glass rod has the same effect as drawing it down in a gas flame. Again, the effect of the absorption of different vapours on the surface has been investigated. Other experiments show that irregularities of the kind postulated are distributed throughout the volume of the material, but that they only become harmful to the strength when they reach the surface.

The statistical distribution of strengths among a number of individual samples is in harmony with the theory, as also is the effect of altering the length of the sample.

The highest value found for the strength of rock-salt is 160 kg./mm.<sup>2</sup> as against the normal value of 0.4 and the theoretical one of 200.

It has been shown that the surface has a deciding influence on the tensile strength both of single crystals and of amorphous bodies. The best way of studying the physical nature of this influence was an investigation of thin sheets and thin fibres, which was carried out by Jurkov and Alexandrov and gave valuable information on the appearance of cracks and discontinuities leading to breakdown.

Since the work of Kwinke it is well known that the tensile strength of thin wires increases as the thickness decreases. The dependence of the strength  $P$  on the diameter  $r$  of the wire can be represented by the formula

$$P = a + \frac{b}{r},$$

just as if the whole load were partly carried by the cross-section and partly by the perimeter. Kwinke assumed that the second effect was due to the surface tension of the solid wire. However, the experimental value of this effect came out about one thousandfold the real surface tension.

Griffith then assumed that a thin sheet of oriented molecules covers the surface of a glass fibre and has a very much higher strength than normal glass. This view seemed to be supported by experiments of Reinkober, who found an increase of elastic modulus for thinner glass fibres.

Jurkov was able to show that Reinkober's results were due to an experimental error. Measuring the stretching of a fibre, Reinkober neglected the displacement of the suspension point. The modulus of glass and quartz came out rigorously independent of the thickness, when this error was corrected.



The following experiments give a conclusive disproof of Griffith's hypothesis: a glass rod of about  $1 \text{ mm}^2$  cross-section was etched in a solution of fluoric acid down to a diameter of  $60 \mu$ . In spite of the removal of the thick surface layer which had been held responsible for the abnormal high strength, the thinner filament had a strength 3 to 5 times larger than the thick rod. The strength of filaments prepared by solution of the surface layer was just the same as that of filaments of the same thickness prepared in the usual way in a gas flame.

The influence of the surface has been best demonstrated by absorption of different vapours on the surface of glass and quartz filaments. Compared with a dry surface strained in a good vacuum, filaments decreased their strength by about fivefold in water vapour, about threefold in alcohol and twofold in benzol vapour. It was also shown that more than one molecular layer is necessary to produce the whole effect.

Dissolving a few microns of the surface layer in fluoric acid, Jurkov found a manifold increase in strength for any thickness of the filament. The dependence of the strength on thickness remained of the same nature both for normal and for etched glass and quartz filaments.

It was thus obvious that the usual weakness of glass and quartz was due to sharp irregularities on the surface of filaments. The next question was whether any such irregularities existed *inside* the glass rod. The tensile strengths of glass filaments have been measured during the process of solution. If faults of the same sharpness were distributed through the whole cross-section, then after a certain time some of them must appear on the surface. As the smoothing of such faults takes place gradually and slowly, while the elastic stresses appearing on a sharp end of a fault spread out with the velocity of sound, we should expect that this would lead to rupture just in the same way as without dissolving. In fact there was no difference between an ordinary filament loaded in air and a dissolved filament loaded in the fluoric acid solution. Even a filament made strong by etching in fluoric acid regained its initial weakness as soon as it was plunged into the same solution.

We conclude from these experiments that faults of the kind responsible for the rupture are distributed throughout the bulk of glass and quartz. They become dangerous however only on reaching the surface.

The mechanism of the growth of surface crevices was studied by Grebenshchikov who showed that the surface of glass is usually covered by a colloidal sheet which swells on absorption of water. In a crevice, the swelling of colloidal silica thrusts the walls asunder and produces a quite measurable stress which was directly observed by Grebenshchikov. In this way every surface crevice is already stretched to a high degree by the colloid; it takes a small additional load to let the crevice grow.

The point of view developed so far does not explain the existence of a definite value of mechanical strength for every material. We should expect the initial irregularities, which give rise to a surface crevice, to be of different sizes and shapes. According to the nature of the initial crevice, the stress necessary to cause it to spread would be different. Thus all strengths, up to the theoretical strength, should

be possible. The explanation is given by the large number and statistical distribution of faults inside a large body.

Just as in the case of Brownian molecular movement, the statistical character of heat motion becomes evident only for very small particles, and statistics of strength can directly be shown on small samples. The shorter and thinner the glass filaments, the larger the fluctuations in the value of strength. Among 100 samples of pyrex glass about  $100\mu$  thick, 1 had a strength of 12 kg./mm<sup>2</sup>; 4 of 15 kg./mm<sup>2</sup>, 14 of 17 kg./mm<sup>2</sup>, 20 of 20 kg./mm<sup>2</sup>, 27 of 25 kg./mm<sup>2</sup>, 18 of 27 kg./mm<sup>2</sup>, 11 of 30 kg./mm<sup>2</sup>, 4 of 35 kg./mm<sup>2</sup> and 1 of 43 kg./mm<sup>2</sup>.

Fluctuations were large in glasses of complicated chemical composition and much smaller in pyrex or in quartz filaments. The number of samples of a given thickness plotted against the value of strength always gave something like a Gauss error curve, which has nothing to do with experimental errors.

The natural hypothesis which explains these observations easily, assumes a variety of faults inside the body. When they reach the surface they give a variety of discontinuities with differing influence on the strength. The most dangerous crevice only is responsible for the observed strength. It is of course natural to assume that the probability of a fault of given sharpness increases with decrease in the size of the fault; thus, there are few very dangerous faults. Loading a big rod with a large surface we expect a large probability of encountering such a fault; the observed strength is therefore always small and most probably of about the value given by the worst faults. The thinner the filament the smaller is the probability of a really dangerous crack on the surface. As the surface decreases, the most probable faults become smaller and smoother, and the discrepancy between the observed and the theoretical strength becomes less. But even among the thinnest filaments there are always found a few samples of much smaller strength. It is clear that the largest possible size of a crevice is limited by the size of the filament. Larger faults have already destroyed the sample before it can arrive at its final thickness. It appears that the fluctuation for the thinnest filament does not reach exactly the lowest limit of a large rod.

From this point of view the length of a filament ought to have the same influence as the thickness. The probability of a given strength is given by the whole surface. In fact the average strength for  $100\mu$  filaments about 5 cm. long was 42 kg./mm<sup>2</sup>, while for 9 cm. it came down to about 32 kg./mm<sup>2</sup>; for  $200\mu$  short filaments we found 22 kg./mm<sup>2</sup> and, for long ones, less than 15 kg./mm<sup>2</sup>.

The average strength of glass filaments for a given thickness is independent of temperature up to the temperature where glass becomes plastic (400–600° C.). From this point the strength decreases and at the same time fluctuations in the values of strength become smaller. The brittle rupture of glass changes into a plastic rupture.

If the explanation given above is correct, we may conclude that the highest values of strength found for the thinnest filaments or for an arrangement where surface crevices are avoided or made ineffective, must approach the theoretical value. It is, therefore, of interest to compare the highest measured value with the expected.

For rock-salt in hot water we have often found 10 kg./mm<sup>2</sup>, in a few cases still more—30 and 160 kg./mm<sup>2</sup>; Piatty observed values of the same order or still higher, while the values of Smekal and his school are somewhat lower (5–6 kg./mm<sup>2</sup>). The theoretical value is about 200 kg./mm<sup>2</sup> and the normal one 0.4 kg./mm<sup>2</sup>. It is quite probable that the rupture of rock-salt is a plastic one. For thick sheets of mica, the highest strength observed by Orowan was 320 kg./mm<sup>2</sup>, while the usual value is 25 kg./mm<sup>2</sup>. For thin sheets Walter found values up to 500 kg./mm<sup>2</sup>. For thin quartz fibres, Jurkov found about 2,000 kg./mm<sup>2</sup> instead of 100 kg./mm<sup>2</sup>; for thin glass filaments 400 kg./mm<sup>2</sup> instead of 10 kg./mm<sup>2</sup>.

These figures seem to show that the theoretical value of mechanical strength may be correct. The practical weakness is sufficiently explained by the Griffith crack theory. The statistical nature of the real strength is in good agreement with this theory.

539-375:548

## THE RUPTURE OF PLASTIC CRYSTALS

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*ABSTRACT.* Sensitive processes start from nuclei (e.g. Griffith cracks for rupture or dust particles for condensation of a vapour). Their sensitivity is caused by two circumstances: (1) The intensity of the external influence (e.g. load or supersaturation as the case may be) necessary to start growth from the nuclei may depend considerably on their size (or quality). (2) The whole process may be initiated by a single nucleus or a few nuclei.—An important difficulty of the crack propagation theory hitherto has been the enormous crack lengths required by the Griffith formula for explaining the technical strength of plastic crystals. Besides the statical notch-effect considered by Griffith, there exists, however, another possibility for the development of cracks by means of plastic slip. By taking this into account, the necessity of assuming unduly large crack lengths can be avoided. Thus the crack propagation theory is to be regarded as satisfactory. On the other hand, proofs are given showing that no secondary or block structure explanation of the technical tensile strength is possible.

THE classical physics of crystals deals with properties which are remarkably insensitive to impurities and physical defects. Thus even if a crystal, embedded in a rock, has suffered considerable alterations by plastic flow of the rock masses, its refractive index and density remain so uninfluenced that very important methods of petrographical analysis can be based upon these properties.

It is easy to understand why these properties are so insensitive. They result from additive contributions of all lattice particles; now if the contribution of an anomalous or anomalously located particle is of the same order of magnitude as that of a normal one and if, besides, the number of anomalous particles is not too large, they cannot sensibly influence the property.

On the other hand, the additivity of a property is not sufficient to make it insensitive if the contributions of the anomalous particles are of a higher order of magnitude. Such a case is represented, e.g., by diffusion in a crystal. Here the particles are held fast in their places by potential barriers; in order to take part in diffusion they must first be set free. If this is effected by thermal agitation, then the number of particles made available for diffusion during a certain time is given

by the Boltzmann expression  $e^{-\frac{E}{kT}}$ , where  $E$  is the height of the potential barrier. This expression in general also determines the intensity of diffusion. For particles which are anomalously located (e.g. at an internal surface) the potential  $E$  is generally lowered, though it remains of the same order of magnitude. If, however,

the temperature is low enough, then the absolute value of the exponent in the Boltzmann expression is so large that a slight decrease of  $E$  can cause an increase of the expression itself—that is, of the intensity of diffusion also—by many powers of ten. So it can occur that in a certain temperature interval the overwhelming part of diffusion is performed by anomalous particles, the process being then sharply influenced by defects and impurities of the crystal.

The mere fact that some properties of this kind can be sensitive in one temperature interval and insensitive in another shows that this sort of sensitivity is not of the very essence of the phenomenon, but can be regarded as an unusually large contamination effect. In many cases, indeed, it is possible to separate the contribution of the defects and impurities and so to obtain, even in sensitive intervals, the value pertaining to the perfect crystal. A very important achievement in this respect has been made recently by Renninger\*. Rock-salt has been regarded hitherto as a characteristic case of an X-ray mosaic structure; Renninger, however, has found that some artificially prepared specimens of it show no trace whatever of a mosaic structure but behave as perfect crystals according to the dynamical theory of Darwin and Ewald.

A particularly simple example of the enormous influence of trivial defects and of the possibility of separating them from the true value for the perfect crystal is presented by the vibration-damping capacity of mica†. Ordinarily, pieces of mica give, if struck, a sound similar to cardboard; thus the vibration damping must be very intense. If, however, by a special kind of very gentle cutting the crushing of the edges into lamellae is completely avoided, then the specimen clicks as clearly as a piece of hardened steel. The great vibration-damping capacity of ordinary pieces of mica is thus almost entirely produced by trivial injuries and not by an inherent system of faults such as would be represented by a secondary or block structure.

Properties of this kind which are of additive character, yet incidentally sensitive because of the great influence of anomalous particles, may be called, for shortness, *semi-sensitive* properties. To this group also belong electric conductivity of semiconductors, X-ray extinction and some photoelectric properties.

In contrast to these, the sensitivity of a third group of even more sensitive properties is, from a theoretical standpoint, of the greatest interest. To this group belong tensile strength, shear strength (in other words, plasticity phenomena), dielectric strength and some properties of ferromagnetic materials. It is easy to see why strength properties are of an extreme sensitivity. The strength of a body is determined by the strength of the weakest part of it; thus a single minute scratch is sufficient to create a weak cross-section in a rod and to lower its tensile strength in extreme cases by tenfold or even more. Because of the decisive rôle of a few of the most critical faults we can appropriately speak of a *selective* character of strength properties, in discriminating them from the *additive* character of the insensitive and semi-sensitive properties.

\* M. Renninger, *Naturwiss.* 22, 334 (1934).

† E. Orowan, *Z. f. Phys.* 87, 749 (1934).

Thus the following classification of the properties of solid matter, and especially of crystals, is obtained:

Property	Insensitive	Semi-sensitive	Sensitive
Character	Additive. Contribution of anomalous parts of the same order of magnitude as that of normal parts	Additive. Contribution of anomalous parts of a higher order of magnitude than that of normal parts	Selective
Examples	Specific gravity and heat, refractive index, X-ray interference pattern, elastic properties	Electric conductivity of non-metallic crystals, diffusion, X-ray extinction, vibration-damping	Tensile strength, plasticity, dielectric strength, magnetization curve of ferromagnetic bodies

As the sensitivity of the semi-sensitive group is of a rather trivial character, the following considerations may be confined to the third group only.

## II

The source of most problems concerning strength properties is the well-known discrepancy between theoretically calculated strength and the actually observed value, which may be called "technical strength." If the law of force between the particles of a lattice is known, then for any given strain the corresponding stress can be calculated. For increasing strain, the stress will have a maximum value which is evidently the tensile strength of the lattice. Such a calculation was made in 1923 for rock-salt by F. Zwicky\* who obtained a theoretical tensile strength of 20,000 kg./cm<sup>2</sup>, which is about 1000 times as large as the actual technical strength of that crystal. In spite of this discrepancy the calculation cannot be incorrect; a second method which is quite different and perhaps less risky, indeed, leads to the same result. This method, suggested by Polanyi, makes use of the surface energy, which is defined as the work necessary to increase the surface of the body by a unit area in a reversible way. For a rough approximation the need of reversibility may be neglected and the surface energy applied for calculating the work which must be performed when by rupture a new surface of known size is created. If, moreover, the assumption is made that Hooke's law holds good until, at the moment of rupture, the stress suddenly drops to zero, then the mutual potential energy between two parts of the body can be calculated; at the moment when during the increase of strain the mutual energy per unit cross-section reaches twice the surface energy, rupture takes place. Hooke's law gives now the simultaneous stress which presents a rough approximation to the theoretical tensile strength. The result for rock-salt is very much the same as that of the direct calculations from lattice theory.

The method of surface energy is applicable in all cases if only an approximate value of the surface energy (whose square root enters into the result) is obtainable.

\* F. Zwicky, *Phys. Z.* 24, 131 (1923).

It is very important that in this way we can calculate the theoretical strength of amorphous bodies and that *here the same discrepancy exists as in the case of crystals*. Even from this fact alone it is rendered most probable that the discrepancy cannot arise from features peculiar to crystals, such as a secondary or block structure.

We may notice that tensile stress has in the case of amorphous bodies the same degree of sensitivity as in the case of crystals. At this point it may also be emphasized that sensitive phenomena are not confined to the crystalline state; they can also appear in amorphous bodies and even in liquids and gases. Thus dielectric strength can be regarded as a sensitive property of gases.

A discrepancy which is quite analogous to that between theoretical and technical tensile strength exists also between theoretical and technical dielectric strength and shear strength of crystals.

### III

Till now, two entirely different possibilities for explaining the discrepancy between theoretical and technical tensile strength have been suggested, viz. the Griffith theory of rupture and the various secondary structure and block structure hypotheses.

According to Griffith\*, the discrepancy is a consequence of the fact that rupture does not take place simultaneously over the whole cross-section of a body, but that it starts from a crack or other inhomogeneity and extends gradually, before the average stress even approaches the theoretical strength. If an absolutely simultaneous rupture along the whole cross-section could be attained, the body would show the theoretical tensile strength. As to the cause of premature rupture, Griffith assumes that the inhomogeneity of stress distribution in the neighbourhood of flaws produces an increase of the average stress in the ratio of the theoretical strength to the technical strength. Thus the theoretical tensile strength is reached at the edge of a crack at the moment when the average stress has the value appropriate to the technical strength. We may assume that the Griffith conception of rupture as a crack-propagation process is to be regarded as proved true. The only addition that must be made in the case of plastic crystals is that here, besides the notch-effect considered by Griffith, another possibility for the premature propagation of cracks must be assumed, namely, a propagation by means of plastic slip. For rock-salt, for example, the depth of cracks required by the Griffith formula for explaining the discrepancy between theoretical and technical strength would be about half a millimetre; for zinc or tin crystals even more. This difficulty of the Griffith theory has played an important rôle in the formation of the various secondary and block structure hypotheses; its solution, however, is very simple. For plastic crystals there exists, besides the statical notch-effect as calculated by Griffith, another possibility for the extension of cracks. This may be explained in the case of rock-salt.

Let  $AB$  be a surface crack in a cube plane perpendicular to the direction of load

\* A. Griffith, *Phil. Trans. Roy. Soc. A*, 221, 180 (1921); *II. Internat. Congr. for Appl. Mech.* Delft, 1924, p. 61.

(Figure 1). If at the point  $C$  in the plane of slip  $CD$  a slip starts, then the parts already slipped pull the other parts of the plane after them until the slipped part is extended to the point  $P$  which is in the continuation of the crack. Now the material remaining between  $P$  and the edge  $A$  of the crack must sustain a stress which is sufficient to transfer the process of slipping to the part  $PD$  below the crack; otherwise it will tear along  $PA$  and the crack will be deepened by the distance  $PA$ . Since we know empirically that a process of slipping is never confined to a single plane but spreads out continuously to the neighbouring planes, in many cases a further deepening of the crack will occur which leads either directly to rupture by a continuation of the same process, or indirectly by a Griffith mechanism, if meanwhile the critical crack depth has been reached.

Now the question arises whether by this mechanism the necessity of assuming very deep cracks can be avoided. The tensile strength of the minute part between  $P$  and  $A$  is evidently very near to the theoretical strength; on the other hand, for obtaining a most unfavourable case, the force necessary to move the triangular piece  $DBP$  must be calculated from the technical shear strength by multiplying by the length of the hypotenuse  $DP$ . By omitting sines and cosines which cannot alter the orders of magnitude, we obtain as a condition for rupture along the line  $PA$

$$PA \cdot z_0 = DP \cdot s,$$

where  $z_0$  denotes the theoretical tensile strength of the cube plane and  $s$  the technical shear strength of the (110)-plane. We take  $PA$  to be several times the lattice distance ( $a = 2.86 \text{ \AA.}$  for rock-salt); since the ratio  $z_0/s$  is about 1000 we obtain for the minimum crack depth  $DP$  an order of magnitude of 1 micron. This is quite a satisfactory value.

We may mention that the formation of visible cracks, evidently by a slipping mechanism, has been observed on several occasions in zinc and rock-salt crystals. So the actual occurrence of this process stands beyond doubt.

The crack propagation theory of rupture accounts not only for the discrepancy between theoretical and technical strength but also for other important features of tensile strength. Moreover it does not encounter any essential difficulties.

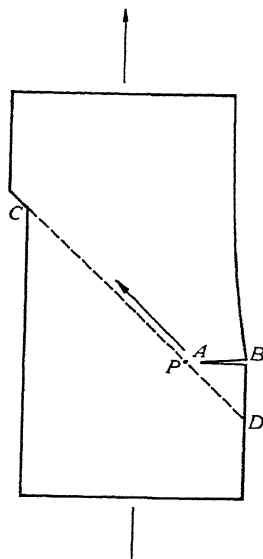


Figure 1

#### IV

A second way, quite different from the crack propagation theory, for explaining the discrepancy between theoretical and technical strength, is presented by the various *secondary* and *block structure hypotheses*. According to these, a crystal is built of very small blocks whose lattice is ideal, showing the theoretical strength as



calculated by means of lattice theory or of a known surface energy. These blocks are, however, separated from one another by layers of disordered particles so that the cohesion between two neighbouring blocks is much lower than its internal strength; it is assumed to be equal to the technical strength of the crystal.

As to the cause of secondary structure, two possibilities exist. The *secondary structure hypotheses* in a strict sense, as pointed out by Zwicky\*†, suppose that the formation of a secondary structure is accompanied by a decrease of the free energy of the crystal; thus a crystal with a secondary structure represents an equilibrium configuration which always results if the crystal remains uninfluenced during a sufficient time. The *block structure hypothesis* of Smekal‡, on the other hand, regards this structure as an inevitable imperfection of the crystal, originating perhaps in the finite speed of its growth. According to Smekal, the equilibrium configuration is given by the ideal lattice; a real crystal would lose its secondary structure if left uninfluenced for a sufficiently long time; this case, however, could not be realized, as otherwise the crystal would obtain its theoretical strength in contradiction to experience.

Zwicky has made two attempts to derive theoretically the existence of a secondary structure. He considered two entirely different arbitrary alterations in the lattice of crystals of the rock-salt type and he tried to show that these alterations would be accompanied by a decrease of the energy of the crystals. If this holds good, then a spontaneous formation of a secondary structure can be expected.

The starting point of Zwicky's first secondary structure hypothesis\* is the fact that a (100)-lattice plane of a crystal of the rock-salt type contracts if set free. According to the calculations of Lennard-Jones and Dent§ the linear contraction amounts in the case of rock-salt to 6 per cent. Though a spontaneous contraction is of course subject to the condition that the plane shall be isolated, Zwicky made the assumption that a contraction of the same amount could also take place spontaneously in the interior of the crystal. He postulated, then, that a minimum of energy is reached when three orthogonal sets of parallel planes are contracted; as to the distance of two consecutive parallel planes, he assumed it to be much greater than the distance of two lattice planes. So the sets of contracted planes would form a secondary structure in the crystal.

For verifying the assumption of the spontaneous contraction of internal lattice planes, Zwicky tried to prove that a gain of energy results from contracting an internal (100)-plane in the ratio calculated by Lennard-Jones and Dent for isolated planes. By calculating the different kinds of energy changes connected with the contraction, he was led in his first detailed paper to the following energy balance:

\* F. Zwicky, *Proc. Nat. Acad. Amer.* 15, 253, 816 (1929); *Helvet. Phys. Acta*, 3, 269, 466 (1930); 4, 49 (1931); *Proc. Nat. Acad. Amer.* 17, 524 (1931).

† F. Zwicky, *Proc. Nat. Acad. Amer.* 17, 524 (1931); *Phys. Rev.* 38, 1772 (1931); 40, 63 (1932).

‡ A. Smekal, *Wien. Anz.* p. 191 (1925); *Ann. d. Phys.* 83, 1202 (1927).

§ J. E. Lennard-Jones and B. M. Dent, *Proc. R. S. A.*, 121, 247 (1928).

Gains of energy:	erg./cm <sup>2</sup>
by the contraction itself	82
by the polarization of ions of the contracted plane and of two neighbouring planes	457
by an accessory change of energy	28
	<hr/>
Sum	567
Loss of energy:	
by increase of the mutual energy between the contracted plane and neighbouring parts of the crystal	500
	<hr/>
Total gain	67

According to this balance, a small gain of energy would be obtained; it is, however, disquieting that the initial gain by the contraction itself is quite unimportant as compared with the other changes of energy and that the total gain represents only a small difference between the two sides of the balance. Afterwards it was found by Prof. Pauling that the calculation of the energy loss was erroneous; the correct value, calculated then by Zwicky himself, amounts to 1140 erg./cm<sup>2</sup>, instead of 500. By this the existence of a secondary structure in rock-salt and also the general existence of a secondary structure of this kind has been proved impossible. Zwicky, however, laid much stress upon the fact that in two cases, viz. PbTe and PbS, even after correction, a gain of energy results. Yet later\* it was found possible to show that the balance contains another miscalculation of a still greater importance. For determining the polarization energy, the electric field strength at the position of every ion must be known. Along the contracted plane or the neighbouring planes, the field strength is represented by products of trigonometrical functions of the two coordinates. Referring to the difficulty of an exact calculation, Zwicky contented himself with calculating the field strength at one particular place and determined the polarization energy by means of this value, declaring that this approximation could not alter its order of magnitude. Now such an approximation is of no use since the total energy change by contraction is given as the difference of two almost equal quantities. Moreover, the field strength assumed by Zwicky was unfortunately just its maximum value; by carrying out the calculation of the polarization energy exactly\*, a value results which is one-third only of the polarization energy obtained by Zwicky (152 erg./cm<sup>2</sup> instead of 457 erg./cm<sup>2</sup>). As the polarization energy represents the decisive part of the total energy gain, this correction converts the balance for every crystal into a large loss. In other words, the calculation of Zwicky shows, if corrected, that *a secondary structure of this sort is impossible*.

An entirely different kind of secondary structure, also suggested by Zwicky†, arises from a generalization of a feature of ferromagnetism. Ferromagnetic bodies possess a spontaneous magnetization, even in the absence of an external field. If the body is, as a whole, unmagnetized, the direction of the spontaneous magnetization must be assumed to vary from place to place, in order to avoid a resulting magnetic moment. Magnetization gives rise to magnetostriction which must likewise vary in different parts of the body, if no saturation has yet been reached. Thus

\* E. Orowan, *Z. f. Phys.* **79**, 573 (1932); **89**, 774 (1934); *Helvet. Phys. Acta*, **7**, 285 (1934).

† F. Zwicky, *Proc. Nat. Acad. Amer.* **17**, 524 (1931); *Phys. Rev.* **38**, 1772 (1931); **40**, 63 (1932).

internal stresses are created, causing deviations from the ideal lattice. A phenomenon which represents an electric analogue to ferromagnetism has been observed by Joffé and his collaborators in crystals of the rochelle salt type.

Now Zwicky has postulated that a spontaneous polarization, either magnetic or electric, is quite a general property of crystals; the accompanying internal electro- or magnetostriction represents a secondary structure which he makes responsible for the sensitivity of strength properties and for the discrepancy between theoretical and technical strength. As an argument in favour of a general occurrence of spontaneous polarization, Zwicky makes a calculation from which he finds that certain crystals of the rock-salt type must show such a phenomenon.

It is perhaps unnecessary to devote a more detailed criticism to this hypothesis as its insufficiency is evident. Firstly, a spontaneous polarization is, as a matter of fact, quite a particular phenomenon whose non-existence can be granted for the overwhelming majority of crystals, especially also in the cases to which Zwicky's calculations refer. Secondly, according to that hypothesis, strength properties should show a complete change at the Curie point or near saturation. So it need only be mentioned as an explanation of the contradiction between experience and the calculations of Zwicky, that the cardinal point in these is the value assumed for the *second derivative* of the repelling force, for which Zwicky uses the simple exponential expression with a repulsion constant obtained as usual from measurements of compressibility. Now Slater\* has shown by measuring the pressure coefficient of compressibility that this expression represents no approximation whatever for the second derivative of the repelling force; so the calculations of Zwicky are illusory.

Although the attempts of Zwicky for deriving a secondary structure in crystals have failed, it could perhaps be imagined that a hitherto unknown third kind of secondary structure exists, producing the principal features of technical strength. Such a secondary structure could be either of the Zwicky type, corresponding to a minimum of free energy, or of the Smekal type (a block structure, caused by inevitable irregularities or by the finite speed of the crystal growth). Now it is of the greatest importance for the theory of sensitive properties that it should be possible, by using some well-known empirical facts, to show in an exact manner that an explanation of the phenomena of technical strength by means of any secondary or block structure hypothesis is impossible. This statement can be proved in the following way†.

If a secondary structure were responsible for the discrepancy between theoretical and technical strength, then approximately the same discrepancy would exist between the theoretically calculated and actually observed values of surface energy. The sphere of action of the molecular forces between two parts of a crystal remains, indeed, practically unaltered on assuming a secondary structure; thus the work necessary for separating two parts of the crystal, in other words, its surface energy, must diminish in about the same ratio as the force, i.e. the tensile strength.

\* J. C. Slater, *Phys. Rev.* **23**, 488 (1924).

† E. Orowan, *Z. f. Phys.* **82**, 239 (1933).

For example, the surface energy of the cube plane of rock-salt, calculated by means of the lattice theory, is about  $90 \text{ erg./cm}^2$ . Since the ratio between theoretical and technical tensile strength is 1000, an observed surface energy of approximately  $0.1 \text{ erg./cm}^2$  is to be expected if the secondary structure hypothesis holds good. Now although an exact measurement of the surface energy of rock-salt has not yet been possible, many approximate measurements have without exception given values of the calculated order of magnitude, in general even somewhat more. A discrepancy amounting to even one decimal place is surely impossible.

Another striking example is given by mica. This crystal possesses an extraordinarily perfect cleavage plane; its tensile strength in a direction perpendicular to this plane must be very small and even the mere preparing of a rod with an axis in this direction would hardly be possible because of the danger of premature breaking. Thus a very low value for the surface energy of the cleavage plane should be expected if the perfect cleavage is caused by a block or secondary structure. Contrary to this, very reliable measurements of Obreimoff\* show that actually the observed surface energy of this plane is about  $5000 \text{ erg./cm}^2$  which is perhaps the highest known surface energy.

These examples are sufficient to show definitely the failure of all secondary and block structure hypotheses. Yet there exists still another argument leading to the same conclusion. If the technical tensile strength of a crystal had to be attributed to a secondary structure, then it could be increased only by altering this structure. Now in the case of mica it is possible to obtain an increase of tensile strength of tenfold by a mere surface treatment. The bounding surfaces of a mica lamella are of two kinds: firstly, two principal cleavage planes of the utmost perfection; secondly, side surfaces forming the edge, which are in general not crystallographic planes and which can usually only be obtained by cutting or grinding. These edge surfaces contain numerous cracks easily observable at a moderate magnification. Thus the assumption that these cracks influence the tensile strength of the lamella according to the Griffith theory is plausible; in other words, that the normal technical strength of mica bands is given by the average stress necessary for the edge cracks to start propagating themselves across the lamella.

That this assumption holds good can be shown by a simple artifice†. If the clamps used for applying the load are narrower than the mica band, then the side borders, being beyond the clamps, bend up at loading and they become nearly stressless so that no propagation of edge cracks can start. In this case the tensile strength of the mica lamella is increased tenfold, a maximum strength of  $32,000 \text{ kg./cm}^2$  having been observed instead of the usual value of about  $3000 \text{ kg./cm}^2$ . Now if the strength of mica in a direction parallel to the principal cleavage plane was determined by the cohesion of neighbouring blocks according to the various secondary structure hypotheses, then it would be capable of no further enhancement, the secondary structure of the individual crystal being given once for all. So this experiment proves directly that the technical strength of mica crystals is determined

\* J. W. Obreimoff, *Proc. R. S. A.*, 127, 290 (1930).

† E. Orowan, *Z. f. Phys.* 82, 235 (1933).

by a system of trivial cracks and that an explanation by means of a secondary or block structure hypothesis is impossible.

A third argument which is less direct but perhaps more impressive is offered by the fact already mentioned that there is no difference between crystalline and amorphous bodies so far as the discrepancy between theoretical and technical tensile strength is concerned. Since a secondary structure is possible only in crystals (if singular cases such as opal are excepted) the block structure hypothesis would attribute a uniform phenomenon to different causes.

By these arguments the impossibility of any secondary or block structure hypothesis is definitely proved. We see that the alternative, whether a hypothetical secondary structure can play an essential rôle in the theory of strength properties or not, is at the present state of things no matter of personal opinion, since the arguments against the secondary structure hypothesis are absolutely decisive. So the principal problem of tensile strength can be regarded as settled: all general features of it are produced by the fact that, according to crack propagation theory, rupture does not take place simultaneously in the entire cross-section but propagates itself gradually, starting from a singular point.

We may yet remark that amongst the defenders of secondary structure hypotheses it has become usual to support their view by enumerating as many empirically known cases of superstructure as possible. It is, however, clear that the very existence of superstructures as, e.g., the X-ray mosaic structure or the Bitter sedimentation stripes on ferromagnetic metals have nothing to do with the question whether a secondary structure plays an essential rôle in originating characteristic features of sensitive properties or not. As a matter of fact, no important case is known where even the individual strength properties of a particular crystal could be brought into relation with a particular superstructure observed in it. For example, the mechanical properties of steel remain practically unaltered on reaching the Curie point, when all superstructures of ferromagnetic origin would vanish. The X-ray mosaic structure can even be regarded as an approach to a polycrystal and thus must cause an increase of tensile strength, since the passage from one mosaic element to another represents a difficulty in the development of a crack.

## V

Till now, we have almost exclusively considered examples concerning the tensile strength. Yet the recent progress of our knowledge on crystal plasticity enables us to derive from it ideas as detailed as those derived from the phenomena of tensile strength; these fit excellently into the picture we have made of a sensitive property in general\*†.

We must omit to deal here with dielectric strength which is, however, so typically connected with a lability of a similar kind to the propagation of a crack, that no secondary structure hypothesis has ever made an attempt to deal with it in a detailed manner.

\* G. I. Taylor, *Proc. R. S. A.*, **145**, 362, 388, 405 (1934).

† E. Orowan, *Z. f. Phys.*, **89**, 605, 614, 634 (1934).

Attention may, however, be called to some sensitive phenomena in ferromagnetic crystals or polycrystals. Recent researches on the origin of technical permeability of ferromagnetic bodies led to the very interesting result that Barkhausen jumps do not take place simultaneously in a certain region of the body but propagate themselves with a relatively low speed\*. As, indeed, R. Becker† has shown theoretically, they cannot result from a continuous turning of the direction of spontaneous magnetization in the direction of the external field, since such a process needs considerably stronger fields than those actually producing Barkhausen jumps. This phenomenon consists, on the contrary, of a gradual displacement of the partition-walls between Weiss regions, in such a manner that a region whose magnetization has nearly the direction of the external field extends itself. According to experiments of Sixtus and Tonks, a stronger external field is needed to start a Barkhausen jump than to continue it; this means that at starting we must overcome a sort of resistance. Considerations on the nature of this resistance have been put forward by R. Becker, Bloch, and Langmuir; it is very probably caused by the smallness of the initial Weiss region, in the same way as extreme smallness of a drop of water checks further condensation on it if the supersaturation is not large. The situation is thus quite similar to the Griffith theory: in the latter the load necessary for continuing the process of rupture decreases rapidly as the area already separated increases; the initial crack forms a *nucleus* for rupture whose size determines the strength.

These considerations lead us to a general characteristic of sensitive phenomena. In all such cases of sensitive phenomena, we have a process which can be regarded as *autocatalytic*; that is, its further development is facilitated if only it has started at a place which we call a *nucleus*. The creation of a nucleus needs a local accumulation of energy either from a material anomaly or from a thermal fluctuation. The amount of external influence (e.g. load) necessary for growth of a nucleus depends in a high degree on the amount of accumulated energy, and on the size and the nature of the nucleus; this great dependence, together with the possibility of spreading out from a single nucleus to a great part of the body, is the cause of the sensitivity.

Thus in the case of the rupture of a rigid body the nucleus consists of a crack which facilitates the process by its notch-effect. The load necessary for propagating the crack is, according to the Griffith formula, inversely proportional to the square root of the crack depth; so the rupture runs on, once initiated, with a high acceleration.

In the case of crystal plasticity, the nucleus is given by a local slip§, originated both by a material inhomogeneity and an additional thermal fluctuation. The local slip facilitates further slipping by producing a zone of dislocations¶ around itself. Very probably the nuclei of Barkhausen jumps, causing the irreversible part of the ferromagnetic permeability, due to displacements of Weiss walls, are produced also by the compound influence of material inhomogeneities and thermal fluctuations.

\* Sixtus and Tonks, *Phys. Rev.* 37, 930 (1931).

† R. Becker, *Phys. Z.* 33, 905 (1932).

‡ G. I. Taylor, *Proc. R. S. A.*, 145, 362, 388, 405 (1934).

§ E. Orowan, *Z. f. Phys.* 89, 605, 614, 634 (1934).

The electric breakdown of a crystal takes place if a single ion acquires a sufficient amount of energy during its movement in the electric field. As the technical dielectric strength is comparatively low, the ion must, for acquiring the necessary energy, have a long path available which is only possible if the crystal contains an imperfection either innate or due to thermal fluctuations. The energy represented by this imperfection can be regarded as the work necessary for creating a nucleus.

We now see that boiling, freezing, condensation, and more generally all changes of phase are to be ranged in a most natural manner amongst sensitive phenomena of a selective character. It will suffice to point to the phenomena of superheating, undercooling and supersaturation; with respect to sensitivity there is no difference between these phenomena and tensile strength, plasticity or irreversible permeability. Their common feature is the rôle of nuclei and the accelerated spreading out of the phenomenon from these. As far as the principle is concerned it is irrelevant whether the nuclei are Griffith cracks, local slips, thermal fluctuations of stress or, on the other hand, dust particles or gaseous, solid, or liquid nuclei produced by thermal fluctuation. We may, however, notice that theoretical strength and condensation-point for example, as defined thermodynamically, are not analogous but opposite quantities: a condensation pressure obtained in a reversible way presumes the presence of very active nuclei; thus it is to be regarded as similar to the highly reproducible tensile strength of mica lamellae, obtained by grinding the edges and providing them in this way with a large supply of cracks\*. The quantity corresponding to theoretical strength in the case of condensation at a constant temperature would rather be the maximum of the van der Waals  $p$ - $v$  curve which is in practical cases cut away by the Maxwell horizontal.

In summarizing the results, we can say that the foundations of the theory of strength properties are to be regarded as clear. The main features of strength phenomena arise from the fact that every breakdown, either mechanical or electrical, starts from minute nuclei which have a decisive influence on strength. On the other hand, an explanation of strength properties by means of secondary structure hypotheses is not only unnecessary but is also impossible.

\* E. Orowan, *Z. f. Phys.* **82**, 247-251 (1933).

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# THE STRUCTURE-SENSITIVE PROPERTIES OF SALT CRYSTALS

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*ABSTRACT.* A structure-sensitive property is one which has different values in different specimens of the same crystal, the actual states of a crystal being of a characteristic metastability. A crystal with structure-sensitive properties must clearly require more variables for its description than the ideal stable crystal, and the simplest model to take is that of an ideal lattice crystal, modified by the presence of gaps of some variability in number and kind.

The observed metastability of the actual crystal for small changes of temperature shows that it really preserves the state in which crystallization occurred.

In the formation of crystals, growth in general takes place tangential to certain definite planes, the molecular character of the growth giving rise to gaps and to local variations in orientation, whilst the presence of impurities leads to the incorporation of foreign atoms. These are all classified as primary flaws, and they are statistically distributed along the principal planes of growth. Secondary flaws are those which result from the alteration of the primary flaws, or from the formation of new flaws in the solid state by mechanical or thermal treatment of crystals. They may reach much greater size than the primary ones.

The relations, statistical and other, to be expected theoretically between flaws and structure-sensitive properties dependent on them, are briefly summarized.

The second section of the paper deals with experimental results obtained on rock-salt, which was chosen for investigation after exhaustive consideration.

It is first shown that the photochemical coloration of rock-salt is a structure-sensitive property, and that by its aid the primary and secondary flaws in rock-salt can be marked.

As an example of general structure-sensitive properties, the strength is then discussed. The experimental determination of the pure macroscopic cohesion and of the elastic limit of rock-salt crystals are briefly indicated. When the connexion between cohesion, elastic limit and crystal flaws is examined, it is found that under mechanical stretching, the first permanent changes occur by local stress concentrations at the flaws, the maximal elastic stresses measured optically being of the order of the ideal lattice strength.

## I. GENERAL THEORETICAL BASIS

### § 1. THE PHYSICS AND STRUCTURE-SENSITIVE PROPERTIES OF CRYSTALS

#### (1.1) *General statement of the problem*

EXPERIMENT gives sharply reproducible results for a large number of crystal properties, which can be satisfactorily explained on the basis of the ideal lattice theory of crystal structure, by means of the atomic-physical properties of the



crystal particles. Other crystal properties are characterized by the fact that they possess different values in different specimens of a crystal, and therefore are *not* describable in terms of the ideal lattice theory, which only permits of *definite single values for crystal properties*. I have contrasted these two groups of crystal properties as *structure-sensitive and structure-insensitive properties*, and have propounded as a task for the more recent crystal physics that it should explain *the simultaneous existence of these two contradictory types of properties in the same crystal*\*. Experimental results show that *cohesion, plasticity, and self-diffusion at low temperatures* are "general" structure-sensitive crystal properties of all materials, so that in each of these cases a *fundamental problem of crystal structure* is encountered. Other structure-sensitive properties, such as the photochemical properties of salt crystals or the magnetization curves of ferromagnetic materials, are confined to special groups of materials and must therefore in all cases be associated with special properties of the material.

### (1.2) *The problem of stability and structure-sensitive properties*

The existence of general structure-sensitive properties indicates that a greater number of variables is necessary for the specification of the state of the crystal than that allowed by the ideal lattice theory or than that demanded by the specification of the structure-insensitive properties. The new quantities introduced must obviously permit only slight deviations from the ideal lattice, which in the general case will have different values from crystal to crystal. The individual, different states cannot therefore possess exactly the same stability. There are then two possibilities:

(a) The absolutely stable condition is the ideal lattice.

(b) The absolutely stable condition is a fundamental state differing in a definite manner from the ideal lattice.

In *both* cases however it is necessary that:

(c) The actual states of the crystal should in general differ both from each other and from the absolutely stable condition; also, on account of the slow rate at which equalization proceeds in the solid state, they should be only temporarily stable but secularly unstable.

### (1.3) *The stability of crystal lattices*

The *absolute* stability of either a finite or an infinite crystal lattice cannot as yet be investigated or demonstrated theoretically. *Electrostatic* systems are of course of a fundamentally unstable nature to which all the criteria of stability so far investigated are inapplicable. Atomic physics and quantum mechanics have shown that the stability properties of a system of atoms are determined by *quantum-mechanical laws*. The full application of these to the crystal lattice is not as yet possible in any

\* A. Smekal, *Proc. Inter. Cong. Phys., Como*, 1927, 1, 181 (Bologna, 1928); *Z. f. Phys.* 55, 289 (1929) and especially "Structure-Sensitive Properties of Crystals" in *Handbuch der Physik*, 2nd ed., 24, (2), chap. 5 (Berlin, 1933) (referred to below as "Structure-Sensitive Properties").

single case. For this, the whole crystal would have to be regarded as built up of atomic nuclei and electrons, full account taken of the spin and exchange coupling, as well as of the electrical, and the ground state of such a giant molecule determined. It is not at present possible to say whether this ground state corresponds to an ideal lattice or deviates slightly from it. Still less is it possible on these grounds to make any assertions as to the nature of the metastable excited states, which are concerned in the case of the structure-sensitive properties.

(1.4) *The point of view of the ideal lattice theory*

The ideal lattice theory assumes the absolute stability of both the finite and the infinite ideal lattice, although this stability cannot be proved. In addition, we can, with Born and Goldschmidt, establish the *relative* stability of the various *simple* lattices, the quantities, sizes and polarization properties of the atoms playing the main determining part. The only variable factor directly reconcilable with the ideal lattice theory, is the *area of the surface* of a finite lattice. Surface components and (internal) lattice components of the crystal possess some fundamentally different properties. Crystals of equal size but with different surfaces must show differences in their properties due to this difference. Since the trivial differences between the outer surfaces of macroscopic crystals are not of importance, there must be *differences attributable to internal surfaces* to account for the structure-sensitive properties. I have accordingly taken as *the simplest model of a crystal with structure-sensitive properties, a crystal built up according to the ideal lattice theory, but containing gaps\**, the secular instability of which crystal as compared with the *ideal crystal* with no gaps needs no further demonstration. In any case there can be no theoretical inconsistency in the ideal lattice theory advancing along these lines towards a basic solution of the general problem (1.1).

(1.5) *The point of view of the instability theory of the ideal crystal*

The hypothetical denial of the absolute stability of the ideal lattice for all crystallizing materials leaves in doubt what are the actual crystal states of absolute stability. A further hypothesis is necessary to fix this state; with regard to crystal symmetry, a reference to the crystallographically defined elements of the general structure-sensitive properties seems to be involved, of which cleavage-, slip-, and twinning-planes as well as the principal direction of self-diffusion in the crystal structure might be selected since they are connected with certain stability properties of the structure. No reason is yet known for the preference for a definite plane or direction from among those enumerated. So far only two general statements of a *negative* character appear to be *demonstrable*: (a) In permanent lattice cells any regular deviation from the ideal lattice reduces the symmetry of the crystal. (b) If in the fundamental ideal lattice, definite planes forming a super-lattice are supposed to be physically changed, it is in general impossible to divide up the original lattice by these planes into congruent blocks if in the super-lattice all the

\* A. Smekal, *Phys. Z.* 26, 707 (1925); 27, 837 (1926), also footnote, p. 94.

planes crystallographically equivalent to one of its planes, behave in an equivalent manner\*. In the case of the secularly unstable states, which according to (1.2) are necessary to explain the structure-sensitive properties of a crystal, a similar reference to external and particularly to internal surfaces in the finite crystal lattice would be essential, as already mentioned under (1.4) in connexion with the ideal lattice theory, so that here also the crystal with gaps appears to be the simplest model.

### (1.6) Zwicky's "secondary structure"

Zwicky postulates the fundamental instability of the ideal lattice in connexion with (1.1), and maintains that the absolutely stable crystal state is an ideal "primary lattice" with a "secondary lattice" of the super-lattice type referred to above†. More detailed description was not given by Zwicky of the nature of the empirical crystal states deviating from this assumption, so that his original views could yield *no* information as to the structure-sensitivity of crystal properties. As to how far his assertions regarding the absolutely stable state may be correct, it is only possible from them to deduce consequences which cannot be confirmed on any single material, on account of the absolute purity and perfection of the structure assumed. A stability *proof* of the fundamental necessity for a "secondary structure" is, as stated in (1.3), just as impossible as is that for the ideal lattice, a fact which Zwicky now admits‡. This being so, any possibility of deducing the secondary lattice corresponding to a given ideal lattice, as e.g. Zwicky has deduced that the secondary structure of the rock-salt lattice consists of the cube faces, becomes impossible. Hitherto Zwicky has not accepted this conclusion and believes that it can be supported by considerations of the electrostatic energy difference between lattices with and without this secondary structure. As stated in (1.3), however, electrostatic energy conditions alone cannot decide problems of stability; moreover we hold with Born and Orowan that the increase of electrostatic energy on the addition of a "secondary structure" claimed by Zwicky rests on faulty analysis§, and does not occur. There is thus at the present moment no certainty as to the instability of the ideal lattice. Other similar computations by Zwicky and Evjen deal with "secondary structures" which are only possible in certain lattices, i.e. selected groups of materials; we refrain from discussing these, as they are of no importance for the problem of the *general* structure-sensitive properties. The only theoretically certain "secondary structure" concerns the distribution of spin in the lattices of ferromagnetic crystals and according to Heisenberg is not of a regular lattice-geometrical nature; it is of considerable importance in the understanding of the special ferromagnetic structure-sensitive properties, but of no fundamental importance in connexion with the general structure-sensitive properties (strength properties) of the ferromagnetic materials.

\* Important examples of theorem (b) are provided by all the regular or pseudo-regular crystals (diamond, rock-salt, aluminium, bismuth, etc.) if the super-lattice is regarded as consisting of the observed octahedral planes established here to be planes of cleavage or slip.

† F. Zwicky, *Proc. Nat. Acad. Amer.* 15, 816 (1929), and later papers.

‡ F. Zwicky, *Helv. Phys. Acta*, 6, 210 (1933), p. 213; A. Smekal, *Phys. Rev.* 44, 308 (1933).

§ M. Born and M. Goeppert-Mayer, *Handbuch der Physik*, 2nd ed., 24 (2), chap. 4 (1933); E. Orowan, *Z. f. Phys.* 79, 573 (1932); *Helv. Phys. Acta*, 7, 285 (1934); *Z. f. Phys.* 89, 774 (1934).

## § 2. THE STRUCTURE AND GROWTH OF CRYSTALS

(2.1) *Permanence of actual crystal states*

The existence of structure-sensitive crystal properties, as in (1.2) (c), implies the existence of individual crystal states, the differences and temporary stability of which are rendered possible by the slow rate at which equalization proceeds in the solid state. It follows from this permanence of the actual crystal states that the states occurring at the conclusion of crystal growth suffer little if any appreciable change in the absence of alterations in external conditions. The most obvious way therefore of accounting for the variety of actual states is to attribute them to the behaviour during growth. Additional more or less easily demonstrable changes in the crystal state can be produced, principally by thermal or mechanical effects, the nature of which changes will then depend on the prior history in the solid state.

(2.2) *Laws of crystal growth*

The laws governing infinitely slow crystal growth of a chemically pure material from a *single centre* have been elucidated by Volmer and Brandes, Kossel and Stranski; the ideal lattice is in this case built up by tangential growth along definite lattice planes of slowest growth, these planes having been calculated by Stranski for several types of lattice. For finite rates of growth the general tangential growth still takes place along these planes; the molecular character of the growth, however, expresses itself in deviations, which are such as to give rise either to the *presence of gaps* in the growing crystal or of *variations in orientation*\*, and which may be considerably assisted, especially by high-temperature crystallization†. The presence of impurities, which can practically never be excluded, leads to the *incorporation of foreign atoms*, in the form, depending on their nature, either of a solid solution or of inclusions (gaps) ‡—in the case of the very small amount of impurities present in the purest materials ( $10^{-4}$  to  $10^{-7}$ ), without any appreciable alteration of the tangential growth along the selected planes of growth. Growth from *several centres* may occur due to excessive supersaturation of the main material or to the exceeding of a definite minimum concentration of specific impurities, the latter particularly in the case of crystal growth from the molten state. The formation of macroscopic “single” crystals by growth from several centres, encourages the development of variations of orientation up to strongly marked (“primary”) “block” structures. All the available evidence seems to confirm the fact that in the case of the purest materials and slowest rates of growth and also for growth from the molten state, fundamentally tangential growth occurs. Further complications in crystal growth are caused principally by spatial or temporal variations in the material available during growth, in which impurities may again have considerable effect.

\* “Structure-Sensitive Properties,” *loc. cit.*, Sections 7 and 8.

† See the recrystallization results of H. G. Müller, *Phys. Z.* 35, 646 (1934).

‡ A. Smekal, *Phys. Z.* 35, 643 (1934), also “Structure-Sensitive Properties,” *loc. cit.*, Section 9.

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‡ A. Smekal, *Phys. Z.* 35, 643 (1934), also “Structure-Sensitive Properties,” *loc. cit.*, Section 9.

(2.3) *Laws of primary crystal flaws*

The deviations from the ideal lattice during the growth of a crystal—gaps, variations in orientation, incorporated foreign atoms—we may call “primary” crystal flaws. In the case of growth from a single centre from material of constant composition both in space and time, the number and distribution of these flaws are determined by the rate of deposition, the temperature and the individual properties of the material of the crystal and of the impurities present. According to (2.2) *the spatial distribution of the flaws is statistically ordered along the principal planes of growth*. The number of flaws in general increases with the rate of growth and with temperature. If these factors are constant, the number of flaws in the same type of lattice is smaller the greater the lattice energy, and for ionic crystals therefore the greater the valency of the components\*. The development of flaws is therefore *under attainable conditions of crystallization* for macroscopic three-dimensional crystals to be considered as just as fundamental a property of the crystalline state as the Brownian molecular motion is of gases and liquids; the flaws can in a sense be considered as a “frozen Brownian motion.” The most important flaws seem to be due to incorporated foreign atoms, especially in crystals with maximum lattice energy (diamond, carborundum); in these substances, the fewest flaws are to be expected in crystals of those materials, for which the strongly unsymmetrical nature of the lattice favours the incorporation of the most diverse impurities in the form of solid solutions, e.g. certain silicates (mica). On the other hand, impurities may in special cases, by stopping most of the possibilities of growth, lead to a very perfect “two-dimensional” crystal growth, from which variations of orientation are practically excluded†.

(2.4) *Laws of secondary crystal flaws*

The result of any alteration in the primary flaws or the formation of new flaws in an already developed crystal will be referred to as “secondary” crystal flaws. Two of the simplest cases are of special importance:

(a) Alteration of the temperature from that of crystallization has the following effects: (a 1) Distortion in the neighbourhood of incorporated foreign atoms *not forming solid solutions*, as a result of thermal expansion of the lattice; these lead either (a 1.1) to local inclusions by self-diffusion or (a 1.2) to local development of mechanical cleavage-, slip- or twinning-planes. (a 2) Supersaturation of the lattice structure with regard to the foreign atoms included as solid solutions; the lattice distortion produced in this way is due to flaws caused by the segregation of the superfluous foreign atoms locally along mechanical cleavage-, slip-, or twinning-planes.

(b) By intentional or unintentional mechanical effects (e.g. mechanical working, cleavage) local cleavage-, slip-, or twinning-planes are formed, and possibly also

\* “Structure-Sensitive Properties,” *loc. cit.*, Sections 8 and 9.

† For more detailed information on this question, see “Structure-Sensitive Properties,” *loc. cit.*, Sections 9 and 23 (c).

slip- or twin-bands running right through the crystal. According to all the evidence, such phenomena are always associated with the development of flaws, distributed along slip zones of finite thickness. At the same time many complications may also occur, with which it is not possible to deal here in greater detail\*.

Special attention must be called to the fact that the flaws formed as in (a 1.2) and in (b) on mechanical cleavage-, slip-, and twinning-planes change in time, even at the temperature of origin and more easily at higher temperatures, by the self-diffusion of particles; which in the case of primary flaws can only occur in materials with very high rates of self-diffusion. The number of newly formed secondary flaws is regularly connected with the intensity of the causative influence. Since the mechanical cleavage-, slip-, and twinning-planes coincide with the planes of the crystal described in (2.2) as the principal growth planes†, *the secondary flaws are statistically arranged about the same planes as the primary flaws.*

### (2.5) *Distinction between primary and secondary crystal flaws*

Whilst primary flaws are characterized in general by their amicroscopic dimensions, secondary flaws may reach such a size as to permit of resolution under the microscope, or even occasionally of macroscopic visibility. Direct conclusive information as to the existence of primary flaws is as stated in (2.4) only possible at the crystallization temperature; indirectly of course, evidence of the presence of insoluble impurities at any temperature is sufficient. The presence of flaws of a size visible under the microscope at temperatures well below that of crystallization always affords good reason to suspect their secondary origin; this can be proved with certainty by observing changes in the flaws, on heating up to the crystallization temperature.

### (2.6) *Layer, block and mosaic structures*

The complete application of the foregoing criteria to the hitherto observed regular layer, block and mosaic structures has not yet been carried out in all important cases. The suspicion on general grounds of the secondary nature of these "empirical" structures can however be brought forward as evidence in the case of the mosaic structure of NaCl and the twin-band structure of KClO<sub>3</sub> crystals. The familiar behaviour of impurities segregated later is observed for the etching properties of Goetz's block structure in bismuth and in the layer structure of zinc, and according to (a 2) implies their origin as in (2.4); the presence of foreign atoms, introduced intentionally, along pseudo-octahedral planes of bismuth has been proved by Goetz and his collaborators by magnetic and radioactive methods. Also the layer structure found by Straumanis in hexagonal metals (Zn, Cd) involves the incorporation of foreign atoms. Finally it should be emphasized that none of these

\* "Structure-Sensitive Properties," *loc. cit.*, Sections 10.

† "Structure-Sensitive Properties," *loc. cit.*, Section 23 (a).



structures possesses exact regularity, but that they rather show only the expected "statistical ordering"\*.

### § 3. CRYSTAL FLAWS AND STRUCTURE-SENSITIVE PROPERTIES

If there is a causal relationship between crystal flaws and the structure-sensitive properties of crystals of a material in the sense of (1.4), then the following very simple conclusions as to those properties which depend on a *large* number of flaws may be drawn:

(a) Different conditions of crystallization give crystals which differ in their structure-sensitive properties, and so provide *proof* of their structure-sensitivity [variation of distribution of flaws as in (2.3)].

(b) The structure-sensitive properties of different individual crystals agree with each other if the conditions of crystallization are kept constant [similarity of primary flaw distribution as in (2.3)].

(c) Similar agreement to that in (b) is shown by crystals with exactly the same conditions of crystallization and previous history [similarity of secondary flaw distribution as in (2.4)].

(d) The structure-sensitive properties of the same crystal can be altered in a regular manner by thermal or mechanical influences, so that the structure-sensitivity even in a single individual is demonstrable [difference between primary and secondary flaw distribution as in (2.4)].

(e) If variation in the structure-sensitive properties is caused by the heat-treatment of crystals with isotropic thermal expansion and not subjected to mechanical treatment, this is due to the effect of foreign atoms [alteration of flaws due to foreign atoms as in (2.4), (a) without other secondary effects].

On account of their dependence on causes which follow *statistical* laws, the numerical values of the structure-sensitive properties of different individual crystals will in general be somewhat different and will possess definite characteristic *frequency distributions*. Consequently we have the following:

(f) The average fluctuation of a structure-sensitive property is smaller the more flaws are causally active and the more similar flaws are available for this purpose.

(g) If a structure-sensitive property depends only on one or a few flaws, large variations in its value may occur.

## II. RESULTS FOR SALT CRYSTALS

### § 4. EXPERIMENTAL PECULIARITIES OF SALT CRYSTALS

At the time when our experimental work on the questions dealt with above was begun, researches of a different nature had already been undertaken by several workers on metal crystals. The chief reasons why we selected salt crystals were:

\* "Structure-Sensitive Properties," *loc. cit.*, Section 10. The super-lattice interference effects to be expected according to Zwicky as in (1.6) in the case of a perfectly regular secondary structure, have not been observed in any case.

(a) the completeness of the theoretical knowledge of the ideal simple ionic lattice; (b) the ease of preparation of salt crystals from a melt and the existence of natural crystals grown nearly at room temperature; (c) the optical check provided by the transparency of salt crystals, as to the intentional or unintentional introduction of foreign atoms; (d) the fact that self-diffusion can be measured by means of the ionic conductivity; (e) the relatively great brittleness and distinct plasticity of salt crystals; (f) the optical and thermal isotropy; (g) the possibility of detecting primary crystal flaws and their alteration due to external influences by photochemical and photoelectric methods (see § 5). So far as is known, no other group of substances unites in itself even approximately as many advantages, as a comparison with the later work of Goetz and his collaborators on bismuth crystals will show. With regard to their structure-sensitive properties, salt crystals are at present the best understood class of crystals, although even here many questions require further work before they can be answered. It is impossible in the following to give a complete survey of present knowledge of the subject\*.

We restrict ourselves therefore to results which for fundamental reasons cannot up to the present be obtained from other substances and which are primarily related to the possibility of detecting primary and secondary structural flaws in crystals.

As far as the *general* structure-sensitive properties and their relation to structural flaws are concerned, it would be expected from the reasons set out in the theoretical section that the results should apply also to crystalline materials of any class.

## § 5. DETECTION OF STRUCTURAL FLAWS IN SALT CRYSTALS

### (5.1) *Wave mechanical basis of photochemical properties of crystals*

According to the wave mechanics of crystal lattices, a locally fixed electron-binding is impossible in the interior of either a finite or an infinite lattice; on the other hand, it is possible at the internal and external surfaces and (what is practically the same thing) also at and in the immediate neighbourhood of foreign atoms which are not present in the form of a solid solution†.

In non-conducting salt crystals, therefore, *flaws in the crystal structure are characterized by locally fixed electron binding*, and can be investigated by means of the particular absorption spectrum of these bindings. Fundamentally, all the (anionic) particles located at structural flaws can be detected by absorption measurements, their concentration relative to the whole number of particles being of the order of  $10^{-4}$  to  $10^{-7}$ . Further, the marking of *definite* flaws in crystal structure is only made possible by the fact that locally fixed electron-bonds can exist solely where there are structural faults; a local metastable excitation of the elements on the inner surface is necessary to secure sufficiently lasting marks without permanent local destruction of the structure of the crystal. In salt crystals, this is attained by the

\* The majority of the relevant papers are dealt with in "Structure-Sensitive Properties" (*loc. cit.*), to which we refer in particular for low temperature self-diffusion.

† "Structure-Sensitive Properties," *loc. cit.*, Section 10 (c). See also A. Smekal, *Phys. Z.* 35, 363 (1934).

photoelectric ejection of the electron from an anion in the flaw, and its photochemical union with a neighbouring cation of the flaw, so that two neutral atoms are formed locally, the absorption spectrum of these atoms making it possible to deduce the number, space-distribution, stability and effectiveness of the structural flaws so marked.

### (5.2) Photochemical marking of amicroscopic structural flaws in rock-salt

The procedure described above has been applied to the various alkali halides and to fluorspar. In the particular case of rock-salt, it corresponds to the amicroscopic yellow coloration discovered by Goldstein in 1896 on irradiation with short-wave ultra-violet light\*, which is due to separated sodium atoms, and possesses an easily measured absorption band in the blue. Electrons are photoelectrically ejected from the sodium atoms by absorption in this band, and after longer free paths, separated chlorine atoms can finally† revert to ions, so that the original uncoloured state of the crystal is restored‡.

All processes for the production of such colours which are not, or are not purely, photochemical (coloration by adding alkali or alkaline earth vapours, by electron bombardment, or by irradiation with cathode rays, X-rays or radium rays) are demonstrably connected with secondary alterations of the structural flaws marked, which in general still remain after the decoloration of the crystal‡. It is easy to convince oneself experimentally by this method that colouring a crystal really depends on locally fixed electron bindings.

### (5.3) Detection of ultra-microscopic structural faults

The photochemical colours are sensitive to heat. If they are replaced by additive colours of sufficient intensity, stable under heat treatment, then the sodium atoms, which are responsible for the coloration, are caused by moderate heat treatment to coagulate into particles detectable by the ultra-microscope. In many cases the particles are arranged in the interior of the crystal along plane or curved intersecting surfaces, so that an otherwise undetectable internal crack system of the crystal is made accessible to microscopic investigation. After internal vaporization and further coagulation, the same ultra-microscopic distribution is obtained, thus proving the definitely localized nature of the crack system§. The demonstration of such crack systems, occurring predominantly in imperfect crystals, by means of the amicroscopic colours from sodium atoms, gives an independent proof that the amicroscopic colours also are associated with structural flaws, as required by the theory|| (5.1).

\* A. Smekal, *Wien. Anz.* p. 195 (1926); *Proc. Int. Congr. Phys., Como*, 1927, 1, 181 (Bologna, 1928); *Proc. 8th Int. Congr. of Photography, Dresden*, 1931, p. 34 (Leipzig, 1932); *Phys. Z.* 33, 204 (1932).

† For the possible intermediate processes, compare Section 10 (b), "Structure-Sensitive Properties," *loc. cit.*

‡ The photochemical detection of changes in secondary flaws has been very thoroughly treated by H. J. Schröder, *Z. f. Phys.* 76, 608 (1932); and K. Helbig, *Z. f. Phys.* 91, 573 (1934).

§ E. Rexer, *Z. f. Phys.* 75, 777 (1932); 76, 735 (1932).

|| A. Smekal, *Proc. 8th Int. Congr. of Photography, Dresden*, 1931, p. 34 (Leipzig, 1932).

## § 6. CRYSTAL STRUCTURE AND PHOTOCHEMICAL COLORATION

(6.1) *Structural sensitivity due to structural flaws*

If the photochemical coloration of rock-salt crystals is investigated under the action of the same number of quanta of ultra-violet light, the coloration being measured by the height of the absorption band at room temperature, then the following results are obtained:

(a) Crystals which are produced under different conditions, give different colorations.

(b) Crystals made under exactly corresponding conditions, give exactly the same coloration.

(c) Crystals prepared in a similar way and with the same history likewise give the same coloration.

(d) The capacity for coloration of a crystal is systematically increased by mechanical treatment.

(e) Purely thermal treatment similarly produces a regular change in coloration.

We see that the photochemical coloration of rock-salt is a structure-sensitive property, and complies in fact with the very simple laws required by § (3), (a) to (e) for a property conditioned by faults of crystal structure.

We have found that the same laws also apply to the structural flaws which are directly demonstrated by the ultra-microscope in the manner explained in (5.3). By the method mentioned, it has been proved conclusively that the photochemical coloration is connected directly with the primary and secondary structural flaws in rock-salt, and that in them, according to (e) and § 3 (e), foreign atoms play an important part\*.

The latter fact receives further confirmation from the increasing capacity for coloration in synthetic rock-salt crystals with increasing quantities of insoluble impurities†.

(6.2) *Distribution and properties of flaws*

According to (5.1), all particles on the inner surface of a crystal can be identified by optical and photochemical methods. That these particles are present in a definitely limited number is shown according to (5.1) not only by the optical method for the uncoloured crystal, but also from the approach to a definite photochemical colour saturation when the ultra-violet irradiation is continued indefinitely. From the time rate of coloration and of decoloration, or from repeated coloration and decoloration, it is generally possible to deduce the nature and stability, as well as the spatial distribution of the flaws in the crystal‡. It is found

\* At a purity of 99.99 per cent to 99.995 per cent of NaCl, the number of foreign atoms and the optically determined number of structural-flaw cations are of only slightly different orders of magnitude.

† Cf. A. Smakula, *Gött. Nachr.* p. 110 (1929); R. Hoffmann, *Z. f. Phys.* 94 (1935); A. Smekal, *Phys. Z.* 35, 643 (1934).

‡ The photochemical detection of changes in secondary flaws has been very thoroughly treated by H. J. Schröder, *Z. f. Phys.* 76, 608 (1932); and K. Helbig, *Z. f. Phys.* 91, 573 (1934).

that the flaws are neither of the same type nor arranged at equal distances, so that with reference to these two factors, there is a definite distribution of flaws for each crystal. The very close accordance between the colours of different parts of a synthetic crystal is due to the very great number (e.g.  $10^{16}$  per  $\text{cm}^3$ ) of colouring atoms, and the identity of distribution properties of the flaws indicated by these atoms. If, however, *just as many* colour-atoms are produced in similar crystals through *different* colouring and decoloration operations, then the difference in the time-rates of their decoloration shows that different distributions of flaws are indicated. It has been shown by similar experiments using heat treatment or mechanical working that the secondary flaws so produced (see (2.4)) are in a markedly unstable condition, and only after a considerable time is a quasi-stationary behaviour reached, consequent on rearrangement of the elements on the internal surfaces\*.

## § 7. MACROSCOPIC STRENGTH LIMITS OF SALT CRYSTALS

### (7.1) *Structure sensitivity of macroscopic strength-properties*

It was emphasized in (1.1) that the strength properties of all materials are structure-sensitive. We have shown by a series of detailed experiments that for natural and artificial rock-salt crystals and for other alkali halides, the very simple *laws* set out in § 3 (a) to (e) *for a property of crystals determined by flaws, are fulfilled at all temperatures*. It is to be specially noted that the strength properties are markedly dependent on the thermal history of the material of the crystal, and that therefore the flaws due to admixture of foreign atoms are concerned in a considerable degree.

Artificial crystals with increasing quantities of insoluble foreign atoms introduced, show regular corresponding changes in strength. For simplicity we confine ourselves in the following to the limits of cohesion and of plasticity under simple tension or compression.

### (7.2) *Macroscopic cohesion of crystals*

The experimental separation of cohesion and plasticity is obtained for rock-salt on cooling to low temperatures†. From about  $-200^\circ\text{C}$ . downwards, rock-salt crystals may be regarded as brittle, so that at these temperatures they are similar to the numerous brittle inorganic crystals. The tensile strength is independent of the cross-section of the crystal and thus measures the macroscopic *cohesion* of the crystal; it is almost independent of temperature and amounts for the purest synthetic crystals, perpendicular to the cube faces, to about  $600\text{ gm./mm}^2$ , with a mean deviation of  $\pm 6$  per cent. This cohesion limit is systematically reduced on the introduction of increasing quantities of insoluble foreign atoms, or by mechanically produced distortion‡. With increasing temperature, the ultimate strength first shows

\* K. Helbig, *loc. cit.*

† A. Smekal, *Z. f. Phys.* **83**, 313 (1933); *Phys. Z.* **34**, 633 (1933).

‡ W. Burgsmüller, *Z. f. Phys.* **80**, 299 (1933); **83**, 317, 321 (1933).

a fall to a minimum (200 gm. mm<sup>2</sup>) at about room temperature, and later rises steeply to a maximum (> 10,000 gm. mm<sup>2</sup>) in the neighbourhood\* of 650° C.

Since this and all the related peculiarities are connected with the occurrence of crystal *plasticity*, which changes the single crystal into a polycrystalline aggregate, we shall only deal in detail with the *commencement* of plasticity.

### (7.3) Macroscopic elastic limit

The stress which produces any fixed small plastic extension decreases smoothly with rising temperature. However, it is quite impossible to determine the "true" commencement of plasticity by any limiting extension defined in this or a similar way. If we define as the "limit of elasticity," that stress at which the first permanent changes within the crystal are detectable, then in general the results will still depend on the sensitivity of the technique employed. If we employ however the properties most sensitive to structure, then we may hope to arrive at lower critical stresses than those that can be determined up to the present. We first investigated this limit carefully at room temperature, and found that by means of the double refraction due to stress† or by means of ionic conductivity‡ we obtained low limiting stresses, but that the determination of a "photochemical limit of elasticity" was the most sensitive method§.

There are here in a noteworthy way two methods which give concordant data: the external stress is determined, above which the tendency to photochemical coloration (§ 6) of an uncoloured crystal increases, and at which a coloured crystal experiences a decoloration|. For the purest unannealed synthetic rock-salt crystals, this photochemical limit of elasticity is 37 gm. mm<sup>2</sup>, at room temperature, for compression perpendicular to the cube faces of the crystal. Crystals with insoluble foreign atoms (SrCl<sub>2</sub>) in the lattice yield exactly the same stress, independent of the content of impurity¶.

The "yield point" determined in compression or tension from the striations due to slip bands on the surface, or from the appearance of the first complete slip planes of the crystal as recognized by double refraction under stress, is, on the other hand, about 150 gm. mm<sup>2</sup> for the pure crystal, and shows a steep increase with increasing content of foreign atoms\*\*.

### (7.4) Plastic deformation on slip planes

The first permanent alterations in the interior of a deformed crystal, according to the foregoing, are of a local nature, since the first complete slip planes recognizable by an external change of form occur at a higher stress. Optical stress measure-

\* W. Burgsmüller, *loc. cit.*; W. Theile, *Z. f. Phys.* 75, 763 (1932); D. Mahnke, *Z. f. Phys.* 90, 177 (1934).

† W. Schütze, *Z. f. Phys.* 76, 135 (1932).

‡ M. Kassel, *Z. f. Phys.* 90, 287 (1934).

§ H. J. Schröder, *Z. f. Phys.* 76, 608 (1932); E. Poser, *Z. f. Phys.* 91, 593 (1934).

| A. Smekal, *Wien. Anz.* 22, 46 (1927); H. J. Schröder, *loc. cit.*

¶ E. Poser, *loc. cit.*

\*\* A. Edner, *Z. f. Phys.* 73, 623 (1932); H. Schönfeld, *ibid.* 75, 442 (1932); W. Metag, *ibid.* 78, 363 (1932); W. Klemm, *ibid.* 94 (1935).

ments on potassium halides\* have explained the intermediate phase as the *formation of local limited slip planes*†, which spread with increasing stress, and finally develop into complete slip layers. In the presence of several crystallographically equivalent slip planes, this pre-growth favours chiefly the slip planes, in the direction which is that of the shortest length within the crystal; this preference is actually observed in artificial rock-salt crystals, and still remains at greater deformations‡. The crystallographic nature of the slip planes produced depends on the relation between the direction of the tension or compression relative to the crystal lattice, as well as on the temperature. In rock-salt, rhombic-dodecahedral, cube and octahedral planes can be slip planes, with the normal to the rhombic-dodecahedral plane as the common slip direction§, whilst the first two mentioned planes can also be cleavage planes. The photoelastic investigations show that the directions of the crystallographic planes merely represent preferred directions, which only agree with the actual slip surfaces within a certain deviation. The origin and course of the actual slip planes are therefore determined by conditions which are not fundamentally crystallographic.

## § 8. STRENGTH PROPERTIES AND CRYSTAL FLAWS

From the experimental data given above (§ 7) and from the results on flaws (§§ 5 and 6) the following relations between the limits of strength and flaws in crystals can be deduced.

### (8.1) *Macroscopic cohesion and flaws in crystals*

Macroscopic crystal cohesion is in general *diminished* by increase of flaws (7.2). The greatest observed diminution, to a quarter of the cohesion of the purest crystal, was produced by a two- to fourfold increase of the flaws. We conclude from this that the cohesion of rock-salt is determined by a *large* number of flaws, which however in view of the considerable dispersion of the experimental results cannot all be distributed in the same way; in fact it has been shown that the formation of the breaking surface mainly proceeds from the surface of the crystal||. A diminution of the macroscopic cohesion by the concentration of stress at hollow flaws is theoretically explicable without difficulty, and is reconcilable also with the theory of the ideal lattice, according to which at the moment of breaking at the critical flaws, stress maxima of the order of magnitude of the cohesion in the ideal lattice are to be expected¶. A calculation of the ratio of the two cohesions (600/200,000

\* W. Schütze, *Z. f. Phys.* 76, 135 (1932).

† The formation of locally limited slip planes has been definitely shown by ultra-microscopic (§ 5) and by optical stress observations to be related to the thermal action of foreign atoms mentioned in (2.4) under (a).

‡ D. Mahne, *Z. f. Phys.* 90, 177 (1934), p. 178; A. Smekal, *Z. f. Phys.* 93, 166 (1935).

§ Cf. E. Rexer, *Z. f. Phys.* 75, 777 (1932); S. Dommerich, *ibid.* 90, 189 (1934); H. Wolff, *ibid.* 93, 147 (1935).

|| Cf. H. Schönfeld, *Z. f. Phys.* 75, 442 (1932).

¶ A. Smekal, *Phys. Z.* 26, 707 (1925); 27, 837 (1926); 34, 633 (1933).

to 400,000 gm./mm<sup>2</sup>) has not hitherto been possible in regard to the mutual actions of a multitude of flaws\*.

### (8.2) Spectroscopic determination of molecular cohesion in crystals

On account of the gradual nature of the failure in tension, there are at the moment when this commences, so few points of maximum stress, that their experimental investigation seems hopeless. This is not the case with compression, where an immense number of cleavage surfaces are formed. We have found that crystals with flaws which are photochemically marked give a shift of the absorption band of about 95 Å. towards the red, at this limit and at room temperature (3000 gm./mm<sup>2</sup> perpendicular to the cube faces)†. This shift is independent of the number of primary flaws, and corresponds to a local increase of energy of  $8 \times 10^{-14}$  ergs. or 0.05 e.v. per colouring atom. In homogeneous elastic strain of the ideal rock-salt lattice, this increase of elastic energy per lattice element corresponds to 300,000 gm./mm<sup>2</sup> perpendicular to a cube plane, which agrees extremely well with the cohesion of the ideal lattice (200,000 to 400,000 gm./mm<sup>2</sup>). In view of the expectation of the general correctness of the ideal lattice theory given in (1.4), this agreement indeed *verifies the order of magnitude of the actual molecular cohesion given by this theory*‡.

### (8.3) Crystal flaws and photochemical elastic limit

From the procedure used to determine photochemical elastic limits (7.3) it follows definitely that the *first detectable permanent changes of a crystal on mechanical deformation occur at the flaws*. The destruction of colouring atoms at the photochemical limit of elasticity yields an energy increase of about  $2.4 \times 10^{-13}$  ergs. or 0.15 e.v. per colouring atom, as estimated by photoelectric and thermal methods§. If this quantity of energy due to the coloration is attributed to an ion-pair in the flaws concerned, then we calculate, in a similar way to the above, that at the flaws there are stress maxima of the order of 350,000 gm./mm<sup>2</sup>. Further, the *commencement of plasticity is thus determined by local overcoming of the ideal lattice cohesion, which spreads out from the positions of these flaws*. The result of this local overcoming of cohesion is in a certain sense observable even in an amicroscopic state, namely by the *increase in the number of flaws*, established by the increasing capacity for photochemical coloration at the photochemical limit of elasticity (7.3). From these facts, it follows that the first changes in flaws must occur in the *flaws of maximum stress*, and that therefore the photochemically determined stress limit actually represents a finite "limit of elasticity." From this it can easily be understood that this limit might be unaffected on artificially adding flaws by introducing foreign atoms: this

\* The only partially verified fracture theory of A. A. Griffith on the fracture of glass assumes single cracks growing with the stress, and leads for rock-salt to a depth of the order of 0.5 mm. for the cracks, which is disproved by the fact that the macroscopic cohesion remains unaltered even down to the smallest cross-sections (0.25 mm<sup>2</sup>).

† K. Helbig, *Z. f. Phys.* **91**, 573 (1934); E. Poser, *Z. f. Phys.* **91**, 593 (1934).

‡ A. Smekal, *Phys. Z.* **34**, 633 (1933); a similar conclusion was reached in *Phys. Z.* **27**, 837 (1926).

§ The numerical values quoted in the last-mentioned work are here corrected by means of a recently published determination of the ratio of the photoelectric and the thermal energies required for ionization (A. Smakula, *Gött. Nachr.* p. 55 (1934)).



must occur for flaws whose properties only permit less than the highest stress maxima. The close reproducibility of the photochemical limits of elasticity ( $\pm 5$  per cent) implies considerable differences of stress maxima in this case, since the experimental determination of the photochemical limit of elasticity demands that there must be permanent changes on at least  $5 \times 10^{12}$  flaws per c.c.

#### (8.4) *The mechanism of plastic deformation on slip planes*

The preceding results give the *local* and *energy* requirements for the commencement (7.3) and the development (7.4) of plastic deformation, which every applicable theory of plasticity must bear in mind, and which must be linked up with *dynamical* ideas. The observed types of slip plane (7.4) find an explanation purely on energy grounds as *planes of minimum energy of molecular separation in relation to neighbouring directions of the lattice structure*, along which the propagation of stress maxima through the crystal lattice occurs most easily\*. The increase of external macroscopic stress required for this follows doubtless partly from the local variations in the inhomogeneity of the distribution of elastic stress at the peaks of stress, and partly from the disturbance of their propagation due to adjacent flaws†. The observed decrease of the elasticity limit and yield point (7.3) with increasing temperature shows further that *heat motion participates energetically in the local overcoming of lattice cohesion, and in the propagation of the stress maxima*. This results from the *influence of the occurrence of high stress maxima on self-diffusion processes within the flaws*: the "energy of separation" of the individual crystal elements is so greatly reduced by the local supply of elastic energy, that their thermal diffusion occurs enormously faster than in a mechanically unstrained crystal; on this account an advance of these stress maxima is possible, which can lie further behind those corresponding to the cohesion of the ideal lattice, the higher the temperature‡. It seems possible§ that such molecular processes, with a slip direction as preferred direction, represent the *fundamental phenomena of plasticity* and cause slip within flawless regions of the lattice; molecular diffusion processes of this kind possess the characteristic dependence on time and non-crystallographic nature of macroscopic plasticity processes, whilst their fundamental reduction at low temperature yields the increasing brittleness (7.2) found here. It is satisfactory that the recent plasticity theory of G. I. Taylor|| has adopted many parts of this earlier work in its basis. As far as I can see, this theory is only in serious disagreement with experience—in relation to the commencement of plasticity and the nature of

\* A. Smekal, *Phys. Z.* **34**, 633 (1933); "Structure-Sensitive Properties," *loc. cit.* section 23 (a), table 19 and section 20 (d).

† The statistical arrangement of flaws about the slip planes which coincide with planes of slowest growth as given in (2.3) and (2.4) is consequently important for the macroscopic strengthening of the crystal.

‡ The qualitative explanation of the temperature-dependence of plasticity due to this cause was stated by A. Smekal, *Phys. Z.* **34**, 633 (1933), and later in a form differing only in externals by E. Orowan, *Z. f. Phys.* **89**, 605 (1934), who dealt in detail with the yield points in metal crystals.

§ A. Smekal, *Phys. Z.* **34**, 633 (1933); "Structure-Sensitive Properties," *loc. cit.* section 23 (a), table 19 and section 20 (d).

|| G. I. Taylor, *Proc. R. S. A.* **145**, 362, 388, 405 (1934).

“hardening”—where its assumptions are different from the above general results. By the direct measurement of molecular crystal cohesion on single atomic particles of the crystal flaws, it seems in any case to have been shown with certainty, that the effect of flaws in combination with the theory of the ideal lattice must be taken into account for an understanding of macroscopic strength properties of crystals.

## DISCUSSION

Dr C. H. DESCH. The evidence for a secondary structure in crystals is not derived from any single property, but is cumulative. Among the facts which lend a strong support to the hypothesis are those concerning the attack of solvents on crystals. That etch-figures arise either from impurities or from convection currents has been disproved, and the regularity of their distribution on uniform crystal faces indicates a periodic structure. The dimensions found for bismuth by Goetz require a unit of  $1.4\mu$ , whilst Belaiew's pits in  $\alpha$ -iron give a cube of  $0.25\mu$  side. In other crystals the unit may perhaps be several microns. A dodecahedral face of a tin crystal gives long parallel ridges on etching, and these ridges are crossed by markings approximately  $2\mu$  apart. Silicon iron gives a coarser pattern, which corresponds very closely with the magnetic pattern recently found by McKeehan to be given by a colloidal suspension of ferric oxide on a magnetized silicon iron crystal. The facts that on deformation slip occurs only on planes many thousands of atoms apart, and that the behaviour of metals on melting and of certain non-metallic substances, such as arsenious oxide, on solution in water, points to the survival of small blocks of the same order of magnitude for an appreciable time, lead to a similar conclusion. The papers read at this Conference make it clear that there is as yet no satisfactory proof of the origin of a secondary structure on this scale, but whatever its theoretical basis, practical experience clearly indicates its existence.

Prof. E. N. da C. ANDRADE. Some experiments carried out by Mr J. G. Martindale and myself throw light both on the stability of the crystal lattice and on the question of faults in crystals, discussed by Prof. Smekal. Thin films of metal, in particular of gold and of silver, were deposited on various surfaces by cathodic sputtering. The surfaces were very carefully cleaned before deposition, and conditions were chosen so as to give very uniform and reproducible films. Particular care was taken to avoid any heating of the films during sputtering. After preparation the films were heated *in vacuo* at various temperatures between  $230^\circ$  and  $600^\circ$ , and the modifications produced were studied microscopically, up to very high magnifications. The microscopic method is inferior to the electron diffraction method in that it gives no direct information as to the spacing of crystal planes, but, on the other hand, it gives information as to local variations of structure and as to crystal boundaries, which the electron method cannot supply. This information can be supplemented by the use of polarized light.

The films, which were about 50 atoms thick, appeared, before heating, perfectly homogeneous under the highest magnification. After heating at  $230^\circ$  C. for an hour

or two the film appeared unchanged to the eye, but under the microscope small specks, varying from about  $0.5$  to  $3\mu$  in diameter, were seen. These, examined in parallel plane polarized light between crossed Nicols, showed as white discs with a black cross superimposed, reminiscent of the rings and cross figure observed with uniaxial crystals in convergent polarized light. The appearance is shown in figure 1, where the magnification is  $\times 5000$ . The arms of the cross are parallel to the planes of the analyzing and polarizing Nicols, and rotate with the Nicols; while rotating the specimen leaves them at rest. This is the known optical behaviour of spherulites, which are spherical masses of fibres of birefringent crystal, arranged radially. The resolution is not sufficient to enable us to decide that the mass is actually spherical—it might be a cone-shaped mass of radiating uniaxial fibres, or a hemisphere. We have here evidence for crystalline fibres radiating from a centre, and that these fibres are birefringent, which is remarkable since both gold and silver, with which the phenomenon was observed, are cubic. The formation of these centres is independent of the surface, and has been obtained with ordinary glass, fused quartz glass, the natural faces of diamond crystals and mica, and also at the free edge of a film, which shows that it is not due to strain. These spherulitic particles have even been obtained on top of a flat silver crystal, by heating a film laid down on top of a first film, which had already been crystallized by prolonged heating.

Further heating, especially at a higher temperature, leads to a growth of the particles, but as they grow they lose their birefringence. The black intersection of the two arms of the cross increases in size, and finally we are left with a well formed cubic crystal, with its (111) face on the glass or crystal surface. Such crystals, which can be grown to sizes from  $4\mu$  to  $15\mu$  across, show birefringence at the extreme edge only. Any particles which do not grow, retain their spherulitic character: any that do, lose it. It would therefore appear that, under the conditions of these experiments, at any rate, the cubic lattice is not stable for particles below  $3\mu$  or so across. The effect is illustrated in figures 3, 4, 5, 6, which show stages of growth in a silver film on silica glass, after successive heatings.

In these crystallizations from the films, the crystalline aggregates are formed very slowly. Another way in which small particles can be formed slowly is by reduction of a solution of the metallic salt in silicic acid gel. Gold particles  $1$  to  $2\mu$  in diameter were prepared by reducing gold chloride in the gel with either sodium sulphite or oxalic acid. These particles, when washed clean and examined in parallel polarized light, showed the same birefringence as the crystalline aggregates in the films, as illustrated in figure 2.

It seems unlikely that a few atoms can maintain themselves in a cubic lattice—clearly less than 8 cannot, and even with  $10^2$  or  $10^3$  times this number there will probably be a tendency to form a spherical aggregate. In the light of these experiments it is suggested that the first stage of crystallization is the formation of such an aggregate, on which many flat ordered faces eventually appear, so that the form is polyhedral. From these faces, columns of ordered atoms grow out, which have an approximately cubical structure, but owing to the relatively small width of the columns, or fibres, compared to the length, the structure is tetragonal, with a small

difference of axial ratio. This would seem to be plausible in view of Lennard-Jones' calculations of the different stable spacing in a plane lattice, and in a cubic

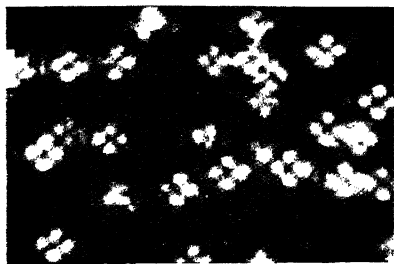


Figure 1. Particles on heated film ( $\times 5000$ )

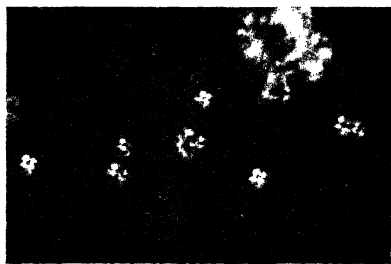


Figure 2. Particles formed in silica gel ( $\times 1650$ )

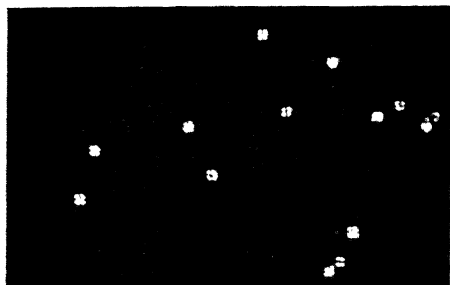


Figure 3

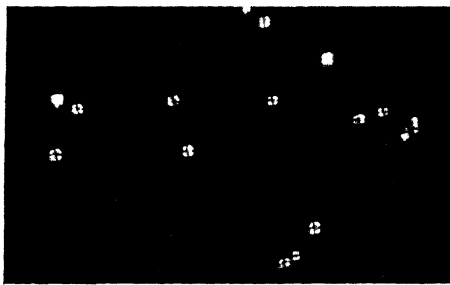


Figure 4

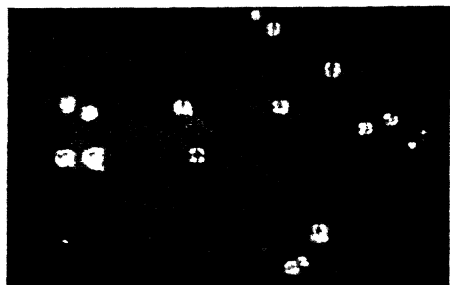


Figure 5

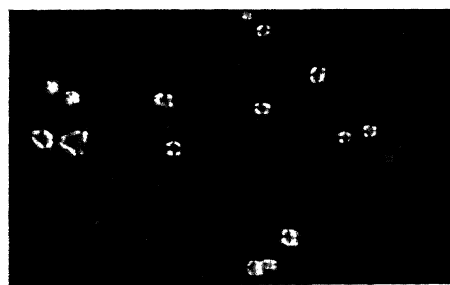


Figure 6

Figures 3-6. Successive stages of growth of particles on heating ( $\times 850$ )

lattice, the tendency, in the case of particles between which van der Waals' forces prevail, being for a wider spacing in the former state. When the number of planes is relatively few and their dimensions are also restricted, some tendency to the wider spacing should persist. As the total width of the spherulitic particles is only a few

thousand atoms, the single fibres may reasonably be supposed to be only a few tens of atoms across, and a few thousand atoms long. If these tentative suggestions are correct the birefringence is explained.

Since prolonged heating never converted a small spherulite to cubic form it would appear that the ideal lattice is not stable for cubical metals below a certain size.

The other aspect of the work to which I wish to direct attention deals with effects produced by the surface on which the film is sputtered. With films prepared on glass surfaces (quartz glass or microscope cover-slips) the crystallites (spherulitic aggregates) showed a tendency to form up in well-defined lines, as illustrated in figure 7. Control experiments showed that these were not due to polishing scratches. To see if the lines could be due to surface impurities the metal film was removed,

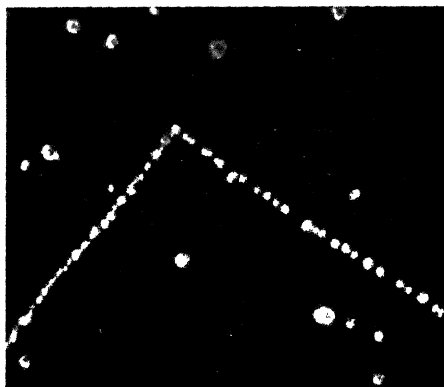


Figure 7. Particles in silver film on silica glass, heated to  $230^{\circ}\text{C.}$  ( $\times 850$ )

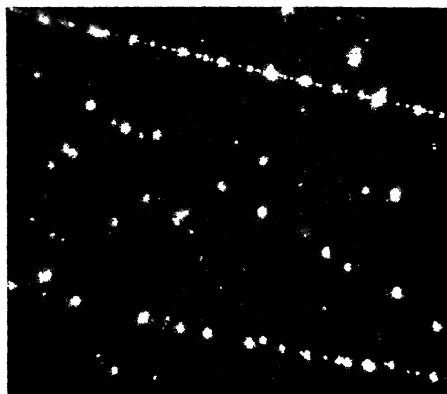


Figure 8. Particles on silica glass, under strong grazing illumination ( $\times 850$ )

the glass carefully cleaned and heated *in vacuo* (at  $550^{\circ}\text{C.}$  in the case of quartz glass), and a fresh film subsequently sputtered on it. This film, on heating, showed an identical pattern of lines, so that the effect survives very vigorous surface cleansing. On the other hand, abrasion and polishing of the surface, estimated to remove a layer  $10^{-6}\text{ cm.}$  thick, abolished the line formation. We concluded that the lines were due to ultramicroscopic surface cracks. Very strong grazing illumination failed to reveal any connecting line between the individual crystallites, as shown in figure 8, so that the cracks must be exceedingly fine.

To verify this, films were prepared on the natural surfaces of diamond crystals. Sir Robert Robertson, J. J. Fox and A. E. Martin\* have shown that two types of diamond exist, for one of which (type 2) a mosaic structure is deduced from their experiments, while the other (type 1) is free from submicroscopic faults. Specimens of each type were lent to us by Prof. W. T. Gordon, and films prepared on natural (111) faces. The usual heating *in vacuo* was then carried out. In the case of type 1

\* *Phil. Trans. Roy. Soc.* **232**, 463 (1934).

there was no tendency for the crystallites to form up in lines, as shown in figure 9\*. With type 2 very well marked lines were formed where no imperfection could be detected by the most rigorous conditions of illumination, as shown in figure 10.

The directions of these lines were measured. They could all be accounted for by

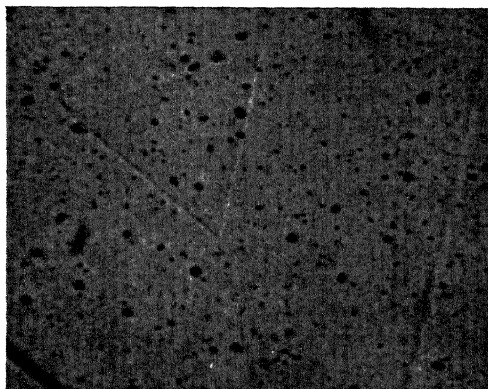


Figure 9. Particles on diamond, type 1 ( $\times 850$ )

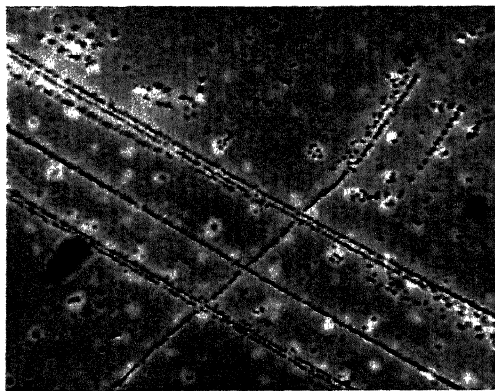


Figure 10. Particles on diamond, type 2 ( $\times 850$ )

intersections of planes, with no index higher than 2, with the (111) face, and one particular set of planes was strongly preferred.

There seems little doubt, then, that the formation of these lines of crystallites in metal films does really indicate surface flaws, too narrow to be detected by ultra-microscopic methods. If this is admitted it follows that these flaws have been directly shown to exist even in the surface of polished silica glass, as demanded by Griffith. The method seems promising, and is being further investigated by me in collabora-

\* The triangle is the outline of a natural surface pit.

tion with Mr F. A. Walch. In particular, we intend to remove the polished surface and look for further flaws.

Referring finally to Prof. Goetz's observations on foreign atoms, the experiments with very pure mercury which I have quoted in the discussion on the final group of papers\* tend to show that impurities play little part in the discontinuities in metal crystals, as evidenced by glide planes. In the first place there will, on these planes, be only one atom of impurity to every few hundred mercury atoms with our purest mercury, and in the second place the spacing of the glide planes is independent of impurity, which agrees with the findings of Prof. Goetz.

Sir WILLIAM BRAGG. It seems to be generally agreed that the "sensitive" properties are due to the existence of a condition which may be described as a series of faults, cracks or discontinuities of some sort. Zwicky has supposed that the discontinuities are regularly distributed in the crystal, being a consequence of the very nature and composition of the crystal. On the other hand, it is maintained that the discontinuities are distributed statistically, being a consequence of the mode of growth or other accidental circumstances. As to the origin of the discontinuities, no theory has been suggested, except that of Zwicky whose arguments in support of it seem to be unsound, and Buerger's interesting theory of lineages.

It may be worth while to consider the matter in the following way. The formula which is taken to represent the forces governing the assemblage of atoms in a crystal, viz.

$$e_1 e_2 \_ A$$

is extremely simple. It cannot provide for all complications. A very natural way of making it more general would be to suppose that the repulsive force represented by the second term is somewhat directive. The effects of such anisotropy would only become evident when the temperature was sufficiently lowered. Thus in a crystal formed at high temperature the atoms would be arranged with geometrical regularity, and the compound would be free of strain. As the temperature falls, strain would enter: if the crystal were cold worked, its atoms would seek a slight readjustment. Let it be supposed that relief can be obtained without altering the general distribution of the atoms; there are to be merely slight changes in orientation and movements which are small in comparison with atomic spacings. This rearrangement will relieve the strain in various regions but will not be able to do so throughout the crystal without interruptions here and there where adjustments must be made involving definite discontinuities of the order of the distances that separate the atoms. Hence would arise the discontinuities of Griffith, Smekal, Joffé, Orowan, Taylor and others. One might compare the effect with that of packing together in close order bodies which were not quite spherical. The packing would proceed regularly for a time with a growing misfit, which would at last require a fresh start to be made.

In this way the crystal would become a mosaic. On occasion the blocks might possess some regularity in size and so account for the observations of Goetz and others.

\* See p. 173.

A crystal formed from the melt would be geometrically regular in the first instance, but would, as the result of cold working, assume the mosaic form in which the blocks had in general lost their parallelism to some extent. This would provide the spacings (which he calls  $L$ ) required by G. I. Taylor. Increase of cold working would increase the extent of readjustment and the prevalence of the mosaic structure, and with that the hardening. Annealing would have the contrary effect.

There is some support for such views in the fact that rock-salt crystals from the melt are geometrically more perfect (Ewald and Renninger) and yet have greater ionic conductivities and are more easily coloured by radiation: which would be expected if the separate atoms are not entirely at ease. And again in Robertson and Fox's two types of diamond, that which is the more perfect geometrically and has less of a mosaic character has more absorption bands than the other.

Again some such effect would account for the limitation in growth of certain crystals, and the persistence of association in companies of a definite order of magnitude that is found on melting.

Dr G. ANTONOFF. The notion of molecular weight has been established as a result of work with gaseous matter, and owing to the Avogadro hypothesis it has become possible to express the same in definite units. Thus, when matter is in a gaseous state, there is a rational method permitting us to determine the molecular weight of a substance experimentally.

But as soon as the material is presented in a state other than the gaseous, nothing definite is known about its molecular state, and the difficulty is in the want of methods for its determination. The substances in the liquid state are believed to be, according to the prevailing view, either "normal," if their molecular weight is said to be the same as in the gaseous state, or "associated" when the molecular weight is supposed to be a certain multiple of that in a gaseous state.

These views, however, are based on a number of empirical rules, whose theoretical foundation is very poor. Besides, their agreement with facts is also highly illusory.

As regards the solid state, practically nothing definite can be said about it. It is even not obvious whether the question of molecular weight in the solid state can arise at all. The X-ray method does not answer the question.

Under such circumstances, it is nowadays realized by some authors that the problem must be solved on quite a different basis, and that some general principle is necessary, a principle analogous to that of the Avogadro hypothesis, which would give a rational solution of the problem for states other than the gaseous.

Assuming with van der Waals the existence of molecular forces, I have deduced some relations which connect the number of molecules per unit volume with other properties of matter.

Imagine a crystal of rectangular form, which consists of molecules at an equal distance from one another. This is represented by dots in figure 1 where each dot represents a molecule. Each molecule is supposed to originate a uniform field of force, no matter what is its nature, which may be different in various cases\*.

\* J. E. Lennard-Jones, *Proc. Phys. Soc.* 43, 461 (1931).



This hypothesis is not the only one possible, but the result obtained remains substantially the same, and independent of the actual form of the law of attraction. For this reason, I limit this investigation to one form only.

Imagine a line  $AB$  in the surface, connecting one row of molecules of unit length. The adjacent rows of molecules will exercise a pull on the line  $AB$ . Consider at first only the forces acting in the surface  $MNPG$  tangentially to it. The effect of molecules situated on one side of the line  $AB$ , summed up together, results in a force  $OC$ , which is generally called the surface tension.

It can be shown in a similar way that owing to the presence of molecules situated below the surface  $MNPG$ , there will be also a pull exercised on line  $AB$  in the direction perpendicular to  $OC$  and acting inwards, represented in the drawing by line  $OD$ . It will be of the same order of magnitude as  $OC$  assuming that the field of force is symmetrical, and will be somewhat bigger, as molecules on either side of the

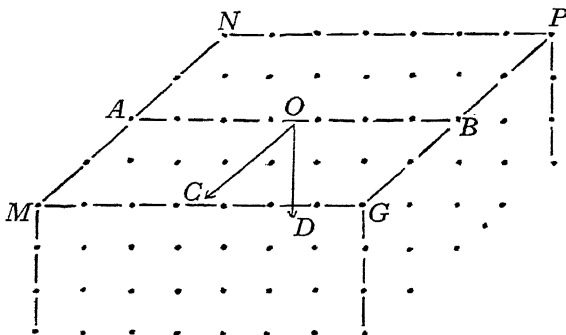


Figure 1

line  $AB$  will act jointly in this case. The field of force, according to the prevailing theories, is of such a nature that the force varies inversely as a high power of the distance.

Consequently in the summing up of the forces due to individual molecules, the adjacent row of molecules will contribute the most important term in the sum. The total force acting on the whole surface  $MNPG$  inwards will be obtained by summation of forces acting on all rows in the surface. This inward force per unit area of the surface is generally called molecular, or normal, pressure.

It thus appears that if the number of molecules and their distance from one another is known, one can easily derive the normal pressure from the breaking stress of the crystal, and thereby also calculate the surface tension.

However, in practice, it is not possible to proceed in this way, as one gets ridiculously low figures from the breaking experiments\*, incompatible with other evidence. This is generally attributed to the fact that the crystal is never perfect and always has small invisible cracks, which diminish the resistance to traction to a considerable extent.

\* Antonoff, *Phil. Mag.* 44, 63 (1922); *Z. f. Phys. Chem.* 102, 388 (1922).

I shall therefore reverse the problem and calculate the inward pressure from the surface tension, which I can measure experimentally by a special method, which is independent of all imperfection in crystalline structure, and which I shall describe later on.

For my calculations I shall use the formula

$$P = K\alpha n^{\frac{1}{3}},$$

where  $P$  is the normal pressure,  $K$  is a constant,  $\alpha$  is the surface tension, and  $n$  the number of molecules per unit volume\*.

In some previous publications this formula was used by myself for calculations assuming  $K=2$  (*Phil. Mag.* **38**, 419 (1919); *ibid.* **44**, 63 (1922); *Z. f. Phys. Chem.* **102**, 389 (1922)). In the case of rock-salt,  $K$  may be put equal to 1.

As regards  $P$  its value derived from breaking stress experiments is generally ridiculously low. Putting the experimental value into the formula, I found for the surface tension of rock-salt the value 1.4 dynes per cm. Such a low value may mean either that the value of  $P$  is so low owing to some imperfection in crystalline structure, or our notion of molecular state is not correct.

As a matter of fact, the data available in the literature (Ostwald, *Z. f. Phys. Chem.* **34**, 503 (1900); Hulett, *ibid.* **37**, 385 (1901)) suggested such values for the surface tension of solids as 4000 dynes per cm.

Assuming the attractions to be purely electrical, I obtained the value 3500 dynes per cm. (*loc. cit.*).

Under such circumstances, I made it a point to devise a method for determination of surface tension of solids, which does not involve the knowledge of  $n$ , the number of molecules per unit volume, and which would not depend on any imperfection in structure.

This I did in the following way (*Phil. Mag.* **1**, 1258 (1926); *ibid.* **4**, 792 (1927)).

I prepared pastes by mixing certain pigments such as lampblack, with inoxidizable oils. I determined the surface tension of these pastes of various concentrations from the breaking stress of their films. With increased concentrations of the pigment, the surface tensions of the pastes increase enormously, and may reach such values as 1000 dynes per cm.

I take advantage of the fact that these pastes wet the solids when their surface tension is small. If one takes pastes with greater surface tension, a point may be reached where the paste ceases to adhere to the solid. At this stage the surface tension of the paste is equal to that of the solid.

This method was checked by a number of experiments with bodies having a low melting point, whose surface tension could be determined by the capillary method in the liquid state. Knowing the temperature coefficient one could see that the method described gives correct results. Thus, I found for the surface tension of rock-salt the figure 315 dynes per cm.

By substituting this figure into the formula

$$P = \alpha n^{\frac{1}{3}},$$

\* This formula was deduced in another publication, see *J. Phys. Chem.* (Sept. 1932).

I calculate  $P$ , assuming

$$n = \delta/M = 2.15/1.64 \times 58.5 \times 10^{-24},$$

where  $\delta = 2.15$  is the density of rock-salt, and  $M$  its molecular weight. I thus obtain:

$$P = 88.5 \text{ kg./mm}^2,$$

which according to this theory is the highest possible value. The experimental figures, except those obtained by Joffé for rock-salt in hot water, are much lower as a rule. I attribute this to the cementing effect of water.

However, the experimental data are very divergent in the hands of different authors. The figures of Smekal and his school do not agree at all with those of Joffé and others, so it is very difficult to draw any definite conclusions at all from the breaking stress experiments.

Taking my own results, there is a considerable difference between the calculated value for the surface tension of rock-salt from purely electrical data, viz. 3500 dynes per cm. and the figure obtained experimentally—315 dynes per cm., of which I am quite sure. The discrepancy between them may mean that weakening of the system is due to the fact that 11 molecules or so combine in some way to a grouping, which in some experiments may behave as a separate unit. If this is so, the normal value for the breaking stress would be about 39 kg./mm<sup>2</sup>.

This is one possibility I can think of in favour of the theory of a secondary structure.

Another theory can be deduced from the laws of equilibrium between different phases of the same substance, i.e. liquid, vapour and solid.

Willard Gibbs found that two liquid phases in equilibrium (i.e. two superposed partially miscible liquids) have the same vapour pressure. This can be also proved experimentally.

Let us call  $p$  the vapour pressure. Then

$$p_1 = p_2 \quad \dots\dots(1),$$

where  $p_1$  is the vapour pressure of one layer and  $p_2$  that of the other, may be described as one of the conditions of equilibrium.

I found experimentally in 1907 that in a state of equilibrium the following law can be stated to be true:

$$\alpha_{12} = \alpha_1 - \alpha_2 \quad \dots\dots(2),$$

where  $\alpha_{12}$  is the interfacial tension,  $\alpha_1$  and  $\alpha_2$  the surface tensions of two saturated layers against their common vapour. I generally call it a "law of difference."

I can also deduce it theoretically. This can be done subject to the condition

$$n_1 = n_2 \quad \dots\dots(3),$$

where  $n_1$  is the number of molecules in the one layer and  $n_2$  in the other.

This relation can be stated to be the third condition of equilibrium.

These conditions (1), (2) and (3) are so correlated that if one of them can be proved experimentally, it automatically involves the others.

The fact that the experimental evidence indicates a full agreement between them, appears to be a proof that the ideal gas laws hold true in such cases. From the fact

that the molecular concentration is the same, both layers must have the same vapour pressure according to Raoult's law. Both layers also have the same freezing point, separating the same ice, and they boil at the same temperature. In other words they are identical in all those properties which depend upon the number of molecules and not their nature.

In an extensive paper (*loc. cit.*) I gave the whole theory, where the above conditions were shown to hold true also for other interfaces.

Thus, I show that liquid and vapour in equilibrium contain an equal number of molecules per unit volume.

At the melting point, when the solid, liquid and vapour are in equilibrium with one another, the same theory must apply.

Thus, the degree of association of the solid at the melting point must be represented by the ratio

$$\alpha = \delta_s / \delta_v,$$

where  $\alpha$  is the factor of association,  $\delta_s$  density of the solid and  $\delta_v$  that of vapour.

The molecular weight will be found by multiplying the molecular weight of the gaseous phase by  $\alpha$ .

The theory set out points to the existence of a secondary structure in one sense. In the mobile equilibrium between the phases, the particles of the solid must detach themselves in groupings of a considerable degree of complexity. Such units may comprise hundreds of thousands of gaseous molecules, according to the evidence in existence. However, if this character manifests itself in kinetic properties, it does not necessarily mean that it will be revealed by all other properties.

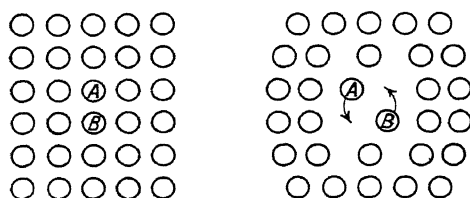
Dr J. D. BERNAL. I should like to draw attention to an aspect of the crystalline state that is not usually considered, namely the fact that at room temperatures most crystals which have been studied, e.g. metals, salts, etc., are not in internal thermodynamic equilibrium.

I have been led to this point of view by considering the relations between liquids, glasses and crystals. A liquid and its glass, in case it forms one, have at any moment the same molecular structure, but a glass, from the very fact that it can be strained and can have different properties according to the heat treatment it receives, is not in internal thermodynamic equilibrium. A super-cooled liquid *per se* is no different from a true liquid. The fact that a crystalline array may have lower free energy at the temperature concerned does not remove the internal stability of the liquid, and there is no discontinuity in its properties at the melting point. There is, on the contrary, a definite change in properties over a range of temperature well below this. Some properties such as viscosity change by enormous factors; others, such as density, hardly change at all. Now there is no reason to suppose that just because in a crystal the arrangement of atoms is regular, similar phenomena will not take place at a temperature below the melting point. A normal crystalline solid may be crystalline in structure but thermodynamically vitreous, able to exist in states of different free energy at the same temperature. The change need not be abrupt, in fact it may be less so than in glasses, but it has already been recognized in the

existence of the recrystallization temperature range above which permanent strain is impossible.

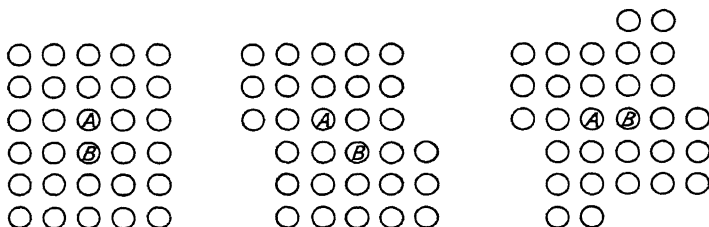
The elementary mechanical theory of crystals strictly only applies when they are in thermodynamical equilibrium, and for processes the time scale of which is comparable with the rate of reaching equilibrium. Incidentally, no theory of crystalline plasticity can be really satisfactory that does not introduce explicitly the idea of a characteristic time.

The high plasticity of crystals above the temperature of recrystallization suggests strongly that they have no true rigidity. If we neglect surface forces, a glide along a



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(a)



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(b)

crystal plane leaves the internal energy unaltered, and requires, therefore, no work but only an activation energy. Now, just as in the corresponding case of electrical conductivity, we must imagine external forces merely to superpose their effect on the spontaneous gliding that takes place without external forces. We have in any case to assume this gliding to account for true crystalline diffusion (apart from diffusion along cracks). It is usually assumed without much thought that in diffusion, atoms change their places, neighbouring atoms simply moving out to let them pass, and then closing in again, as in the upper part of the figure. The activation energy of such a process is much too great to occur in a crystalline solid. The amount of disorganization required is only compatible with the liquid state.

It is much more probable that diffusion takes place by repeated spontaneous

gliding along different planes, as shown in the lower part of the figure. Such spontaneous gliding gradually diminishes with temperature, as does the diffusion, until below a certain temperature both are imperceptible. The forced gliding that occurs at lower temperature when the crystal is internally "glassy" must be of a different nature. I think that for this Prof. G. I. Taylor's mechanism, or some variant of it, is the most plausible. As it stands, however, it contains a paradox. The fewer the dislocations the weaker the crystal, but a crystal with no dislocations would be infinitely strong. However that may be, the dislocations probably exist at high temperatures as fugitive singularities which are "frozen" in at low temperatures, more or less appearing according to the rate of annealing. Once there, they cannot disappear and can only be made to move by external strain.

Dr J. BRENTANO. The fact that the mosaic structure is not a constitutional property of rock-salt, which results from Prof. Ewald's measurements on large crystals, is also found for smaller crystals obtained by distillation. I prepared crystals of about  $10^{-3}$  cm. side by the slow distillation of chemically pure sodium chloride in a vacuum and found that the intensities of their X-ray reflections corresponded within 10 per cent with the intensities expected from perfect crystals. Mechanical grinding increased the intensities of reflection and brought the crystals into an intermediate state between perfect crystals and mosaics. The comparison of the intensities after grinding, with those from powders of chemically precipitated sodium chloride, sufficiently fine to give no appreciable extinction, showed however that the process of mechanical grinding is inadequate to break up completely the regular lattice of the crystals originally obtained by distillation.

Dr W. G. BURGERS. The following considerations (compare A. E. van Arkel and W. G. Burgers, *Polytechn. Weekblad*, **28**, 547 (1934)), although not applying directly to the lattice-deviations considered in Prof. Smekal's paper, may perhaps be of interest in connexion with the question whether there exists any correlation between a definite structure-sensitive property and the "character" of the "lattice-irregularities" by which it can be influenced. For metals and alloys this seems to be true at least to some extent, as can be deduced from a study of the sharpness and intensity of their Debye-Scherrer interference lines. So, for example, the well-known fact that the electric resistance of an alloy, giving sharp Debye-Scherrer lines, is in general much higher than that of the pure components, shows that this property is influenced by "lattice-irregularities" of the order of the atomic distances, thus being of extremely small "period." On the other hand, the stresses required for an increase in coercive force, probably require regions of "homogeneity" of the order of magnitude of  $0.5 \mu$ , as seems to follow from the fact (see for example W. A. Wood, *Phil. Mag.* **13**, 355 (1932)) that in this case a broadening of the Debye-Scherrer lines is often observed. Hardening, again, may perhaps be connected with irregularities of smaller period. In fact, strongly cold-worked aluminium, although exhibiting a considerable hardening, shows no appreciable broadening of the Debye-Scherrer lines (see U. Dehlinger, *Z. f. Krist.* **65**, 615 (1927)), whereas cold-worked tantalum, while exhibiting a pronounced broadening

of these lines, shows neither marked hardening effects, nor a pronounced increase in electrical resistance (W. G. Burgers and J. C. M. Basart, *Z. f. anorg. Chem.* **216**, 223 (1934)). Similar conclusions can be drawn from papers by G. Kurdjumow and G. Sachs on the hardening of carbon-steel (*Z. f. Phys.* **64**, 325 (1930)) and by J. Hengstenberg and G. Wassermann (*Z. f. Metallk.* **23**, 114 (1931)) on age-hardening of duralumin. Especially during ageing of definite alloys it is well known (for example W. Köster, *Stahl u. Eisen*, **53**, 849 (1933)) that the various physical properties considered above often do not vary simultaneously, which fact again points to the possibility that they are influenced by lattice-irregularities of different "periods."

M. F. CANAC. The so-called plane surface of a solid consists in reality of an assemblage of elementary crystal faces each with an area of several square microns, forming polyhedral "holes" or "humps." The light scattered from the surface is due to reflection on these minute faces. The distribution in space depends on the number and the size of those faces which are in a position to return the light in a given direction. If the corresponding relations are determined, simple photometric measurements suffice to give the "mean topography" of the solid.

If the facets are all parallel, the surface is perfectly polished. If they are distributed equally in all directions, the holes or humps will on the average be spherical. We are thus led to study reflection from a plane covered with little reflecting spheres, or dotted with reflecting hemispherical holes. It is found by calculation and verified by experiment that such a plane scatters light with the same intensity in all directions, subject to the obvious condition that the rays are not stopped by the edges of the holes or by the surfaces of the spheres. The deviations from this law depend on the extent to which the individual holes deviate from the mean.

If the surface is formed by hollows which are approximately hemispherical but which have on their surfaces other smaller holes or humps of the type mentioned above, then the light scattered in a given direction is of the form  $(A - B i)$ , where  $i$  is the angle of incidence of the beam.

If the surface has deep cracks with walls which diffuse as in the previous cases, the scattering is of the form  $(A - B \tan i)$ .

By illuminating surfaces at various angles, and measuring the distribution of scattered light, I have traced the scattering indicatrix for the different surfaces. The predictions are more nearly verified, the closer the holes approach to their mean.

In this way I have been able to verify them in a precise manner on many specimens of alloys. In this way each of the three types of surface mentioned above has been found to exist, the type with deep cracks occurring particularly for inter-crystalline corrosion. The method allows us to follow the process of corrosion, to discover the form of the resistant parts of the solid, and to form an idea of their structure.

Finally, it may be mentioned that when the faces have a preferred direction (lamination), this also can be brought out clearly by the method.

Dr J. A. DARBYSHIRE. I was interested in the little spherulites which Prof. Andrade described as existing in the thin films of sputtered gold and silver. During

the course of some experiments on electron diffraction we were passing a beam of high speed electrons (30–36 kV.) in a normal direction through thin films of cadmium oxide in which there were small crystals of metallic cadmium suspended in some way in the oxide film. We obtained well defined spot patterns which we tried to interpret as two-dimensional cross-grating effects in a manner similar to the interpretation usually given to the cross-grating patterns formed when a beam of electrons passes through very thin mica. We found many difficulties in such an explanation and it appears more likely that the effects are due to aggregates of little crystallites somewhat similar to the spherulites of Andrade but with a great many of the side chains stripped off, leaving a cone of chains about the direction of the beam as axis, that is, normal to the plane of the film.

Prof. G. I. FINCH. The study of surfaces by the method of electron diffraction has brought to light the fact that the normal crystal structure of a surface film can be profoundly modified by the nature of the substratum upon which the film has been formed. For example, G. P. Thomson<sup>(1)</sup> found that the orientation of the crystals of a silver film was that of the silver substratum upon which they had been formed by electro-deposition. My collaborators and I have also observed a similar effect in the case of platinum films formed by cathodic sputtering on to a crystalline platinum substratum. An even more remarkable demonstration of how eagerly even a foreign atom may enter into the building up of an ordered crystal structure is afforded by the phenomenon of basal-plane pseudo-morphism<sup>(2)</sup> as shown, for example, by aluminium (normally face-centred cubic,  $a=4.05$  Å.) which when deposited in a thin layer on platinum (face-centred cubic,  $a=3.91$  Å.) acquires a face-centred tetragonal structure,  $a=3.91$  Å.,  $c/a=1.03$ ; thus in this case the platinum substratum imposed its basal crystal dimensions on the aluminium without, however, affecting the normal spacing of the aluminium lattice in the direction of the  $c$  axis. Phenomena such as these testify clearly to the urge impelling newly arriving atoms to continue extending a structure rather than to start building a new one; and if the block structure in crystals is sub-microscopic then the underlying cause of such discontinuity must indeed be powerful. Prof. Lennard-Jones has just suggested that lattice contraction due to electrostatic forces in small ionic crystals might produce the effect. Quite recently Dr Wilman and I<sup>(3)</sup> have redetermined by electron diffraction the lattice dimensions of zinc oxide using gold as a standard for reference. Whilst our value for  $c/a$  agrees excellently with W. L. Bragg's for zincite<sup>(4)</sup>, our  $a$  and  $c$  values are about 1 per cent higher than his. Now, the crystals we examined were exceedingly small, probably appreciably less than 100 Å. in length; further, the binding forces in zinc oxide crystals are probably mainly atomic and not electrostatic, and in such a case, according to Lennard-Jones' theory, the lattice dimensions should increase with decreasing crystal size. Thus Lennard-Jones' theory appears to afford a reasonable explanation of the high values found by us for the zinc oxide lattice constants.

We are continuing our experiments with a view to determining the effect, if any,



a useful contribution and adds force to the observations of Joffé in so far as it shows that the breakdown of crystalline materials can occur as the result of quite minute surface defects.

Apparently, however, the theory as described only applies to single crystals. In multigranular metals like iron and its alloys as we find them in practice, the breakdown first occurs in crystal grains in which the slip planes are favourably directed in relation to the stretching force. For breakdown to occur from a surface defect it would appear necessary therefore that the defect should occur inside one of these particular crystals.

In Dr Orowan's paper, page 83, considerations seem to be based on Hooke's law but this appears to have a very limited range of validity in single crystals, in which the elastic or proportional limit is very low indeed.

Dr A. JOFFÉ. The important contribution of Sir Robert Hadfield raises the problem of applying results and considerations drawn from the study of single crystals and glasses, to a multicrystalline metal.

Now there is a fundamental distinction between brittle glass fibres on the one hand, and cold-worked and drawn metal wires on the other, these at room temperature and the usual rates of loading being in a plastic state. The influence of the thickness is partly explained by the hard-worked layer of a metal wire. Nevertheless I should think that sharp inclusions are responsible to a considerable degree for the actual strength of a wire.

Again, both steel and quartz become brittle at the crossing point of the curve for the yield point and that for the strength. (The X-ray method gives the value of the yield point and not of the elastic limit, which is very low for single crystals.) It seems that the yield point of nickel and nickel alloys does not increase, or only increases slowly, when the temperature decreases. Unlike the case of carbon steel, there may not be a crossing point at attainable temperatures.

Finally, the marked difference between manganese steel and iron may be due to the phase changes taking place during the cold working of manganese. Austenite is often transformed into martensite with accompanying change of magnetic properties. Moreover, the low elastic limit of quenched manganese steel is less important for the rupture than the yield point, which seems to lie higher.

Dr E. OROWAN. 1. I am very glad that a remark of Sir Robert Hadfield gives me an opportunity to call attention to the fact that the plastic crack-propagation mechanism is also applicable to internal cracks. In my paper, I considered surface cracks only, because of their practical importance; we know, indeed, from experience that rupture starts actually in most cases from a surface crack. It is, however, easy to see that an internal crack can be propagated in exactly the same way as a surface crack, if a set of slip-planes near its edge comes into action. At the same time, the stress at the opposite part of the edge increases, because of the widening of the crack; thus a plastic propagation of an internal crack can also lead to a rupture by a notch-effect.

2. Both the notch-effect mechanism of Griffith and the plastic mechanism of

crack-propagation, apply directly to a single crystal or to a single grain of a polycrystalline body only. For the rupture of multigranular bodies, such as technical metals, a second criterion must also be fulfilled: namely, the crack, after having spread across an unfavourably directed or located grain, must penetrate into the adjacent grains. Because of the different lattice orientation of different grains, the passage of a crack beyond a grain boundary generally needs a stress which is considerably higher than that necessary for propagation within a single uniform grain. This is the cause of the high strength of multigranular bodies as compared with single crystals\*.

3. As to the very limited range of validity of Hooke's law in single crystals, this is caused exclusively by intervening plasticity phenomena which are not essentially connected with the elastic strain; so their occurrence does not imply a failure of Hooke's law, just as the burning out of an incandescent lamp on reaching a certain voltage does not signify that the law of Stefan and Boltzmann becomes invalid beyond this critical temperature. Thus the use of Hooke's law for calculating the order of magnitude of the theoretical strength, as suggested by Professor Polanyi, must be considered as correct.

Dr B. LOCKSPEISER. I should like to ask Sir William Bragg whether the model put forward by him involves surfaces of discontinuity within the crystal, dividing parts of the crystal of different energy contents from each other.

Sir W. BRAGG. It would be a probable consequence of my suggestion that a mosaic crystal and an ideal crystal would have different energy contents. So far as I know, however, heat of dissolution has never been found to be a "sensitive property." But the degree of sensitivity might be small, because the changes in position and orientation, which I have assumed tentatively, are small and the energy change which they involve might be small also, even though the forces were large. Thus the regions on two sides of a discontinuity might have different energy contents if they differed in mosaic character.

Dr E. OROWAN. In his Opening Survey, Sir William Bragg pointed out that a difficult problem of the crack-propagation theory of tensile strength is given by the question, how from the action of accidental cracks a more or less sharply defined strength can result. That accidental cracks can produce a sharply defined strength at all, has been proved in the case of mica. The ordinary tensile strength of mica lamellae is determined by cracks on its edge (see E. Orowan, *Z. f. Phys.* 82, 235 (1933)). Now lamellae with a ground edge show a tensile strength which can be reproduced within a few per cent (*loc. cit.* p. 249 and figure 6) and so belongs to the most sharply defined tensile strengths known. Thus the question, how accidental cracks can give a definite tensile strength, is, of course, a difficult problem, but no difficulty for the crack-propagation theory.

The explanation of this problem given by Prof. Joffé in his paper "On the Mechanism of Brittle Rupture" is strongly supported by the fact that the strength of mica lamellae with a ground edge is much more sharply defined than that of

\* Cf. E. Orowan, *Z. f. Phys.* 86, 200 (1933).

lamellae which have been cut with scissors. Since the number of cracks is much greater in the first case, a better reproducibility of the strength must be expected according to the views of Prof. Joffé.

In a footnote at the end of his paper\*, Prof. Smekal asserts that the temperature-dependence of plasticity, as derived by myself from the Becker formula, differs "only in externals" from a form given previously by him. Contrary to this, my conception of plasticity is radically different from that represented by Prof. Smekal; moreover, in my paper (*Z. f. Phys.* **89** (1934), footnote on p. 657) I showed that his fundamental assumptions are inadmissible.

Prof. A. SMEKAL. Contrary to Dr Orowan, I must insist on my statement, that his interpretation of the temperature-dependence of plasticity differs only in externals from mine. The fundamental fact, that plasticity processes start or proceed always on crystal flaws with local stress maxima of the order of magnitude of ideal lattice cohesion—which we proved by rock-salt experiments—is adopted by Orowan without alteration. Again, Orowan uses the assumption that the thermal energy demanded for this process is greatly reduced by the local supply of elastic energy of the stress concentrations on the flaws. Indeed, only these two facts are required for a qualitative understanding of the temperature-dependence of plasticity. In my papers it is stated that the effective elastic energy concentration belongs primarily to single particles of crystal flaws. On the contrary Orowan desires to use the Becker formula, which concerns only homogeneous strain within finite volumes of flawless, ideal lattices; Orowan assumes that homogeneous strain within finite volumes of lattice may be realized also at the actual crystal flaws, so that the elastic energy supply belongs according to him to a multitude of particles. Obviously this assumption is in contradiction to stress concentration on the flaws, necessarily connected with inhomogeneous stress distributions around the flaws, giving the maximum stresses on single particles. The claim of Orowan, that he has shown the inadmissibility of my fundamental assumptions on a diffusion mechanism of plasticity, seems to be just as erroneous, as his criticism disregards all decisive arguments.

Sir ROBERT ROBERTSON. I might amplify the remarks made by Sir William Bragg and by Prof. Andrade on the subject of the two types of diamond that have been discovered by my colleagues and myself.

The failure to give an absorption band at  $8\mu$  in the infra-red in the case of one particular diamond, and its much greater transparency in the ultra-violet when compared with a large number of diamonds all of which gave a large absorption band at  $8\mu$ , led to an investigation of the physical properties of the two types, an account of which will be found in *Phil. Trans. Roy. Soc. A*, **232**, pp. 463 to 535. (See also *Nature*, **134**, 485 (1934).)

Besides being more absorptive, the ordinary type is more anisotropic and has very much less photoelectric conductivity than the less usual type. Both types have in common the same Raman difference, dielectric constant and refractive index.

A large electric current is produced with the less usual type, by the imposition of short length ultra-violet light (max.  $\lambda$  2300). A diamond thus activated responded to green or red light (max.  $\lambda$  5850), even after it had been kept for a considerable time in the dark; but if in the meantime light of wave-length of  $\lambda$  2400 to  $\lambda$  5000 had been imposed on the diamond previously activated by light of  $\lambda$  2300, no response was obtained by the red light.

It was observed that this photo-electric effect occurred in diamonds which appeared to be laminated. Indeed, the search for others, five now having been obtained, was conducted by looking for such diamonds as were obviously finely stepped. A coarse stepping is common among natural diamonds, but this was of no importance.

As has been shown on the screen by Prof. Andrade, the photo-conductive diamonds are those which he has shown by his technique to be more striated than the ordinary sort.

In the paper referred to, the comparatively easy production of photo-electric currents is considered to be connected with the mosaic structure of these stepped or laminated crystals, the atoms at the boundaries of the irregularities being thought to lose electrons more readily than those in the uninterrupted lattices. It was therefore of great interest to see the model produced by Sir William Bragg to account for these irregularities in the major structure of diamond.

Prof. A. SMEKAL. I should like to give some additions and corrections to the papers of Joffé. There are or were many differences of interpretation and also differences concerning experimental facts. We have repeated a number of the experiments of the Joffé school and have found somewhat different results. For simplification, it will be sufficient to deal on this point only with the strength of rock-salt crystals. Contrary to Joffé, rock-salt has no standard strength, neither in air<sup>(1)</sup> nor in water<sup>(2)</sup>, nor in vacuum<sup>(3)</sup>. The strength is not independent of temperature<sup>(4)</sup> nor of velocity of deformation<sup>(5)</sup>. Lastly, rock-salt is not brittle at ordinary temperature, but possesses a characteristic plasticity<sup>(6)</sup>. On other points we are in agreement with Joffé, namely on facts which were found and published in my laboratory before the Russian school, for instance on the increase of faults by plastic deformation<sup>(7)</sup>, on the photoelectric determination of limit of elasticity<sup>(8)</sup> and on the existence of a kind of dissociation along the gliding planes.

Concerning his experiments for the realization of the theoretical lattice strength, Joffé now agrees that his results are plasticity-effects. His original aim of realising the lattice strength on a brittle state of a crystal therefore could not be established. I hope it is now generally accepted from these experiments that the rise of the strength to the order of magnitude of the lattice strength results from the destruction of the monocrystalline state by plasticity.

Special reference is necessary to the statements of Joffé on rock-salt crystals where the surface was dissolved by water. In his paper Joffé speaks only of solution during loading experiments and claims that he has disproved my water-penetration explanation of the watering plasticity, by experiments on partially protected crystals

given by Classen-Nekludowa. But the lack of penetrated water on the protected side must prevent the rise of complete gliding planes, necessary for the ordinary watering-plasticity of crystals; the observed fact, that the strength remains unchanged in this case, is then by no means inconsistent with the water penetration theory. Moreover, the presence of water in the interior of dissolved crystals was demonstrated spectroscopically by Barnes. A saturated solution of salt gives neither solution- nor strength-effects in solution. On the penetration theory, contrary to the opinion of Joffé, only very slow penetration, or no penetration at all, of water molecules into the rock-salt is expected in this case.

The statement of Joffé that our own experiments had changed my opinion on my theory is incorrect. We have recently made dissolving experiments without mechanical deformation of crystals and have measured the effect of watering on the strength, after drying the surface with concentrated alcohol<sup>(9)</sup>. Wendenburg, in my Institute, used different solvents and found different after-effects, clearly connected with the different dipole-moments of the solvent molecules<sup>(10)</sup>. Roeber, also working in my Institute, has found that the after-effect increases systematically with the time of solution, and exhibits very interesting changes with the time which elapses between drying and carrying out the mechanical experiment. The strength of crystals decreases first to a minimum situated above the strength of undissolved crystals, then it rises to values much higher than the initial<sup>(11)</sup>. All these observed facts are consistent only with a penetration theory, which seems in this way directly established.

Another point of difference is the statement of Joffé that the practical weakness of crystals cannot be influenced by internal faults. This statement can only be accepted in a very restricted form, as we have proved by experiments on rock-salt crystals with various foreign atoms. If we suppress the plasticity of rock-salt by means of very low temperature, the strength is generally diminished by increase of internal flaws<sup>(12)</sup>.

Crystals with as many faults as rock-salt exhibit fine-stepped cleavage planes by interferometric observation, and so make it directly visible that the strength is influenced by a great number of internal flaws<sup>(3)</sup>. Only in the limiting case of crystals with few faults is the influence of flaws situated on the surface naturally predominant, as Joffé has indicated. Experiments of the late Lord Rayleigh and more recently by Bond and by Siegbahn on cleavage strips of mica have given only a few steps and prove then the presence of only a few internal flaws for these crystals. In accordance with this fact, the strength of mica found by Orowan is only ten times less than the expected value of the theoretical lattice strength<sup>(13)</sup>.

There is no doubt that the splendid experiments of Griffith on the strength of glass and his theory of the breaking stress have been the most striking suggestions for all later experiments on the strength of glass and crystals. I would like to express my agreement with Griffith that his treatment of a single flaw of elliptic cross-section was and is only the first step to a general theory of stress-concentration in bodies with any flaws and its relation to breaking stress problems. This generalization seems to be necessary because all quantitative applications of the Griffith

theory, excepting only his original experiments, are not in full accordance with experimental facts. I should like to indicate here only the breaking of glass rods. Our experiments gave, contrary to Joffé, breaking surfaces, which often started from internal flaws<sup>(14)</sup>, and breaking stresses, depending for certain glasses on temperature<sup>(15)</sup>. The most striking point is this. The breaking surface of glasses consists of a smooth mirror-like part and another uneven part. For rods of the same cross-section, and under the same conditions of experiment, the mirror-like part is found of very different magnitude<sup>(16)</sup>. On the Griffith theory the breaking surface should always be mirror-like over the full cross-section. We see, also, that the breaking process in glass never depends on a solitary surface flaw.

What I said on these facts refers also to various statements in Orowan's paper. In connexion with my name, this paper deals with matters which were not given by me and for which I am not responsible. In particular, I have never proposed a block theory of strength, of the type indicated by Orowan<sup>(17)</sup>, which is completely contradictory to our own experiments. To establish this it should be sufficient to compare Orowan's paper with mine.

#### REFERENCES

- (1) F. BLANK. *Z. f. Phys.* **61**, 727 (1930); H. SCHÖNFELD, *ibid.* **75**, 442 (1932).
- (2) U. HEINE. *Z. f. Phys.* **68**, 591 (1931); G. F. SPERLING, *ibid.* **74**, 476 (1932).
- (3) W. BURGMÜLLER. Thesis, Halle, 1935.
- (4) W. BURGMÜLLER. *Z. f. Phys.* **80**, 199 (1933); **83**, 317 (1933).
- (5) G. F. SPERLING. *loc. cit.*; D. MAHNKE, *Z. f. Phys.* **90**, 177 (1934).
- (6) F. BLANK. *loc. cit.*; W. THEILE, *Z. f. Phys.* **75**, 763 (1932).
- (7) A. SMEKAL. *Wien. Akad. Anz.* **22**, 46 (1927).
- (8) H. J. SCHRÖDER. *Z. f. Phys.* **76**, 608 (1932); A. SMEKAL, *Phys. Z.* **34**, 633 (1933).
- (9) A. SMEKAL. *Wien. Akad. Anz.* (1928), p. 62; *Naturwiss.* **16**, 262 (1928); *Phys. Z.* **32**, 581 (1931).
- (10) K. WENDENBURG. *Z. f. Phys.* **88**, 727 (1934).
- (11) J. ROEBER. *Z. f. Phys.* 1935 (in course of publication).
- (12) W. BURGMÜLLER. *Z. f. Phys.* **83**, 317 (1933).
- (13) A. SMEKAL. *Handbuch der Physik*, 2nd ed. **24**, 2, pp. 919-20 (1933).
- (14) K. H. H. MÜLLER. *Z. f. Phys.* **69**, 431, § 4 (1931).
- (15) K. H. H. MÜLLER. *loc. cit.* § 7.
- (16) K. H. H. MÜLLER. *loc. cit.*; G. APELT, *Z. f. Phys.* **91**, 336 (1934); G. THIERBACH, *ibid.* **91**, 344 (1934).
- (17) Orowan also fails to indicate the *ideal* connexion between lattice blocks, mentioned in one of my oldest papers, and making this conception equivalent to the gap crystal model.

Dr A. JOFFÉ. I should like to avoid a discussion of Prof. Smekal's declarations of priority and of the historical development of the investigations on rock-salt. I do not deny that some of my ideas suggested by our investigations of rock-salt in the years 1919 to 1923 were changed by new experimental facts found both in my laboratory and by the school of Prof. Smekal.

As far as I can see, the objections of Prof. Smekal can be summarized in the following four statements:

1. The strength of rock-salt depends on temperature.
2. Rock-salt is already plastic at room temperature.
3. The high strength of wet rock-salt is only due to plastic deformation.

4. Wet rock-salt becomes plastic by penetration of water and not by a change of the surface.

1. It may be that the approximate constancy of the brittle strength of rock-salt (within  $\pm 10$  per cent) is not present in samples of different origin. The strength curve may be somewhat concave in those cases. All that is essential for my presentation of a brittle and plastic state is a crossing of this curve with the steep curve representing the dependence of the yield limit on temperature. In no case is it permissible to combine in one curve the brittle rupture at low temperatures with the plastic rupture at high temperatures. Similarly, Smekal's curve representing the strength at a given velocity of deformation between liquid air and  $+500^{\circ}\text{C.}$ , or a curve of "Dauerfestigkeit," is meaningless from a physical point of view. These are different systems of representing measurements, which may become useful when some new physical idea has appeared. If Prof. Smekal could realize at higher temperatures the value for brittle rupture as the lower limit of the strength at increasing velocity of deformation he would find my results with more or less accuracy.

2. It is true that the elastic limit of annealed rock-salt is as low as  $10\text{ gr./mm}^2$ , while rupture occurs at  $300\text{--}400\text{ gr./mm}^2$ . It is also true that by exceedingly slow deformation during 100 hours I was able to bend a rock-salt crystal under room temperature. Nevertheless the rupture of rock-salt at room temperature at ordinary conditions can be regarded as a brittle one, as it appears before the yield point shown for instance by X-ray asterism and by the flow of material is reached. Both pure brittle rupture and plastic distortion are limiting cases (important, as I tried to show, for the understanding of the physical phenomena leading to a breakdown). Though there is a continuous change from one to another, at a definite stage of this change we meet a new situation, where the essential features become different. Changes produced by gliding below the yield point do not alter the obviously brittle character of the rupture of dry and cold rock-salt.

3. The high strength of rock-salt measured in water is observed in an already plastically deformed crystal. The essential point is however the high magnitude of the cohesion forces, leading to a high strength when secondary phenomena are avoided. This is shown to be true whether we deal with single crystals like quartz and mica, with multicrystalline bodies like rock-salt and steel, or with an amorphous material like glass or amorphous silica. In all cases we do actually increase the strength by suitable treatment of the surface and the theoretical strength is the more nearly reached the more completely all secondary influences are removed.

4. I am sorry if I have misunderstood one of the various statements made by Prof. Smekal\*: "Whether the high plasticity of wet rock-salt can find sufficient explanation by these results (penetration of water), I regard as uncertain." Prof. Smekal then suggests two other explanations which agree with my statements in the only essential point, namely, that water eliminating surface disturbances leads to a markedly higher tensile strength. As the yield points of dry and wet rock-salt are equal, it seems that some increase of strength by removal of surface imperfections

\* *Phy. Rev.* 43, 306 (1933).

must be assumed in order to understand how the plastic flow of wet rock-salt starts. Both the absence of any influence of saturated salt solution and the experiments of Classen-Nekludova and Davidenkov show that surface conditions are important for this first step in the plasticity of rock-salt crystals in water. From hundreds of samples taken from a water bath, some lost their plasticity after a few seconds and some after many days. How could water disappear from all the imperfections inside the crystal during a second?

I did not understand the explanation of the experiments of Classen-Nekludova given by Prof. Smekal. Why did not water penetrate from inside to the protected strip after solution of the greater part of the crystal? The experiment shows that a small dry spot on the surface is more important than the penetration of water into the crystal.

New experiments on this subject mentioned by Prof. Smekal should be very interesting and should help us to understand the influence of water on rock-salt, but I do not think they will alter the fact that a change of the surface conditions is essential for the rupture, just as it is in the case of glass, steel and quartz.

Dr E. OROWAN. 1. Prof. Smekal asserts that, in connexion with his name, my paper deals with matters which were not given by him; he writes: "In particular, I have never proposed a block theory on the strength of crystals, which is completely contradictory to our own experiments."

I must, however, maintain the statement that Prof. Smekal suggested the block-structure hypothesis, referring expressly to the problems of mechanical strength, especially to the discrepancy between theoretical and technical strength. In his paper referred to in my contribution, he wrote\*: "Bestehen die Gitter der wirklichen Krystalle hingegen aus sehr zahlreichen submikroskopischen, im Sinne der Bornschen Theorie ideal-regelmässigen, nahezu gleich orientierten 'Gitterblöcken,' welche das Zustandekommen von Störungszonen und Porenwegen ermöglichen, so gelingt es, die aufgezählten Schwierigkeiten [amongst other things, the discrepancy between theoretical and technical strength—Orowan] zu überwinden, ohne damit auf die bisherigen Erfolge der Bornschen Gittertheorie verzichten zu müssen.—Bezüglich der Festigkeitseigenschaften der Krystalle ergibt sich vor allem die bereits früher angegebene Aufklärung der niedrigen 'technischen Festigkeiten' . . ."

This paper of Prof. Smekal was, as a matter of fact, the starting-point of a block structure explanation of mechanical strength as described in my paper, which became very widely spread in the subsequent years, especially amongst mineralogists and metallurgists, without being disavowed by Prof. Smekal himself until now. The experiments he refers to were performed later and published without pointing out that they are in contrast with the common views on block structure hypothesis.

2. Recently I showed† that the penetration hypothesis of the Joffé effect, as advocated by Prof. Smekal in his contribution to this discussion, cannot be main-

\* *Wien. Anz.* p. 192 (1925).

† *Z. f. Phys.* 86, 210 (1933).



tained. A simple calculation, using an experimentally determined lower limit for the speed of solution of rock-salt in water, gives an upper limit for the depth at which water becomes practically saturated when penetrating into invisible crevices of such a crystal. This upper limit is  $1/10$  mm. if a saturation amounting to 999/1000 is required. Since a surface layer of 0.4 to 0.5 mm. at least has to be dissolved before an appreciable increase of strength appears, the interior of a crystal showing the increased strength has never been in contact with solution other than saturated. Now it is well known that immersion in a saturated solution does not produce any trace of a Joffé effect; thus this effect cannot be caused by a penetration of the solvent into the interior of the crystal but by a surface action only\*.

This inference is supported by the following observation of Wendenburg (*loc. cit.*): If a sufficiently thick surface layer of an unloaded rock-salt crystal is dissolved, then after drying the crystal shows a Joffé effect of the usual order of magnitude. Its strength diminishes somewhat in course of time; yet it reaches asymptotically a final value which is still of the same order of magnitude. Obviously the only explanation of the Joffé effect which is in accord with this behaviour is that given by Joffé himself (removal of surface cracks by solution as the cause of the effect). That the strength obtained and the final strength vary slightly with the nature of the solvent is considered by Wendenburg and by Prof. Smekal as a support to the penetration hypothesis. This standpoint, however, seems to be forced; it is, indeed, a very general feature of etching, which plays a fundamental rôle in metallography, that the coarseness of an etched surface depends upon the nature of the solvent.

The fact that there is, besides, a connexion between the increase of the strength and the dielectric constant of the solvent, is also considered by Prof. Smekal as a support to his hypothesis. This influence is, however, most probably due to the fact that the strength of a body is *lowered* if a fluid penetrates into its cracks, in consequence of the decrease of its surface energy by adsorption†. This means that the action of the penetrating fluid is inverse to what is supposed by the penetration hypothesis.

Mrs C. F. TIPPER (Miss ELAM). I should like to give two examples of structures in crystals which seem to support Goetz's experimental results and are related to yesterday's discussions.

1. The first illustrates the laminated structure produced on a polished surface of copper when a fully annealed specimen is heated *in vacuo* at  $950^{\circ}$  C. A similar structure was described by Rosenhain in silver some years ago. The laminations are definitely related to the crystal structure and very much resemble slip-bands. On the other hand they are frequently curved, even in fully annealed material.

2. The second refers to the etch figures on calcite. The size of the etch figures

\* The objection made by Wendenburg (*Z. f. Phys.* **88**, 727 (1934)) emphasizing that a saturated solution may not penetrate at all into the crystal is obviously unsafe; with his assumption, the penetration hypothesis would *a fortiori* be illusory.

† Cf. E. Orowan, *Z. f. Phys.* **86**, 206 (1933).

produced by dilute hydrochloric acid on the surface of a cleavage rhomb differs from crystal to crystal. When such a rhomb is twinned mechanically in the manner described by Baumhauer, the size of the etch figures is much smaller on the surface of the twinned portion than it is on the original surface. This indicates a breaking-up of the crystal structure, although crystallographers state that the twinning is perfect.

Dr A. E. H. TUTTON. As one of the "old gang," to which Lord Rutherford referred at the morning session, I am very glad to learn that Prof. Ewald has succeeded in obtaining the perfect crystal of sodium chloride, and that he has found it to afford the data which he has expected, and which fulfilled the predictions of Prof. Darwin for the perfect crystal.

We have heard much to-day concerning "Krystallbaufehler," and also much of late concerning the "ideally imperfect" crystal, the "mosaic crystal," which has answered so admirably the purposes of the X-ray rotation method of crystal analysis. I myself have been combating for many years the "mosaic crystal," so unsuitable for crystal measurement and crystal optics. For of the 36 years which occupied me in the work on the rhombic sulphates and selenates of the alkalies, and on the monoclinic double sulphates and selenates containing  $6\text{H}_2\text{O}$ , quite half the time was taken up in preparing perfect crystals, affording crystal angles true to within one minute of arc, free from mosaic or any other imperfections, by using only material of perfect chemical purity, and eliminating all sources of disturbance, thermal or otherwise. Often as many as a hundred crops of any one of the 91 salts were prepared, and only one or two found adequately perfect for my purpose and used in the investigation. Hence, it is possible for me to have a very special appreciation of Prof. Ewald's success, and a great satisfaction that it has afforded such excellent results in confirmation of theory.



# PLASTICITY AND STRAIN HARDENING IN CRYSTALS



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## SHEAR HARDENING AND RECRYSTALLIZATION OF ALUMINIUM SINGLE CRYSTALS

WITH AN APPENDIX ON "TRANSFORMATION HARDENING"

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**ABSTRACT.** The paper is a review of an extensive series of investigations on the deformation and recrystallization of aluminium crystals.

It is pointed out that when a crystal undergoes plastic deformation it is hardened, the shear resistance increasing considerably. All recent theories on the origin of this effect agree that the macroscopic glide process consists essentially of the combined effect of a large number of "local glide steps," which are related to the deviations from the ideal lattice structure.

A homogeneous shear distortion can be produced in a circular disc cut out of an aluminium single crystal plate if it is compressed with certain precautions. Nevertheless, Laue photographs show the presence of "curved" lattice regions, the curvature having a definite crystallographic direction. This implies that slip has occurred over *limited* regions of the slip planes.

Again, if gliding occurs along more than one set of planes, then local curvatures occur along each operative system.

The picture thus formed of the inner structure of a "homogeneously" deformed single crystal can be, at least partially, confirmed by studying the recrystallization process. In fact, the nuclei for the small crystallites formed by recrystallization occur at the local curvatures of the glide planes, so that the crystallites occupy a definite preferred orientation determined by the glide processes which occurred during the deformation. Moreover, if two crystals have undergone the same shear hardening, one by shear along a single glide plane, and the other by shear along more than one, then there is a difference in recrystallizing power; there are less nuclei in the case where more glide planes have been in operation.

In an experiment which illustrates this, aluminium single crystals were stretched 10 per cent parallel to the [100] and others parallel to [110] direction. Measurement showed that their hardening was practically the same, but on recrystallization, there were practically no crystals formed in the first case, whereas, in the other case, the crystals became fine-grained. This agrees with the fact that in the first case the local curvatures are smaller than in the other, implying that the total shear has then been divided over more glide planes.

The appendix deals with transformation hardening, which occurs on transition of one phase of a solid metal into another. Here the new lattice is formed from the old by a homogeneous deformation consisting of one or more simple shears combined with small dilatations or contractions. It differs markedly from the processes previously considered, in that, in this case, the transformation process may cause the specimen to become harder, unlike a strained test-piece, which becomes annealed on recrystallization.

IN the present paper a review is given of the results obtained during the years 1928–1933 in a series of investigations on the deformation and recrystallization of aluminium crystals, the details of which have been published elsewhere.

(1) It is a well-known fact that the “strength” of an undeformed crystal is of a lower order of magnitude than would be anticipated from theoretical considerations regarding the forces which hold the atoms or ions in crystalline lattices together. Such considerations have been put forward especially by Joffé, Smekal and Zwicky\* for ionic crystals like rock-salt, and by Polanyi and Schmid† for metal crystals.

If, however, a crystal undergoes plastic deformation, it hardens, the hardening process effecting an increase of the shear resistance of the not-hardened crystal from its extremely low value to a value, which, at its highest, is of the order of magnitude anticipated from the above-mentioned theoretical considerations regarding the atomic forces.

Several theories‡ have recently been put forward to account for the above-mentioned characteristic features of crystalline plasticity. They may be said to have in common the fundamental conception that the macroscopic “glide process” consists essentially of the combined effect of a large number of “local glide steps,” the occurrence of which is closely related to the presence, even in the undeformed crystal, of some kind of deviations from the “ideal” lattice structure. Although the various theories differ apparently regarding the exact nature of these deviations (“Lockerstellen” (Smekal), “dislocations” (Taylor), “Versetzungen” or “Verhakungen” (Polanyi; Orowan, Dehlinger)) and as to the way in which they initiate slip (as a consequence of local stress concentration or of special conditions of potential energy), their conceptions agree in so far that local glide steps occur under the influence of shear forces, which, while being originally small compared to that expected for an “ideal” lattice, increase with the number of deviations§.

The hardening process is, therefore, essentially connected with the increasing distortion of the deformed crystal. In case a crystal is subjected to a shear deformation, which, as to its *outer* form, is homogeneous over its full extent, this distortion must be related in some way to the “limited” character of the individual glide steps. The knowledge of the “internal distortion” of a “homogeneously” deformed crystal is thus important for the understanding of the glide phenomenon as a whole. It is the object of the present paper to show that some insight into this state may be obtained from a study of the recrystallization of single crystals which have been deformed in this way.

(2) If we cut a circular disc out of an aluminium single crystal plate (see Laue photograph, figure 3 a), and compress it between flat steel blocks with all necessary

\* A. Joffé, *The Physics of Crystals* (1928); A. Smekal, *Phys. Z.* **34**, 633 (1933); F. Zwicky, *ibid.* **24**, 131 (1923); *Helv. Phys. Acta*, **3**, 269 (1930).

† M. Polanyi, *Naturwiss.* **16**, 1043 (1928); M. Polanyi and E. Schmid, *ibid.* **17**, 301 (1929).

‡ A. Smekal, *loc. cit.*; G. I. Taylor, *Proc. Roy. Soc. A*, **145**, 362 (1934); E. Orowan, *Z. f. Phys.* **89**, 605 (1934); M. Polanyi, *ibid.* p. 660; K. Yamaguchi, *Sci. Pap. Inst. phys. chem. Res. Tokyo*, **11**, 151, 223 (1929); see also U. Dehlinger, *Ann. d. Phys.* **2**, 749 (1929).

§ In *Proc. Acad. Amst.* (“Report on Viscosity”, Chapter v) is a suggestion how to combine the theories of Taylor and Orowan.

precautions for minimizing the resistance between blocks and disc, in the manner described by Taylor and Farren\* (polishing and greasing of the disc, etc.), this disc takes an elliptical shape, indicating that, from a macroscopic point of view, a *homogeneous* shear deformation has taken place, in the way illustrated by figure 1 for a single glide plane.

This is confirmed by taking *rotation* photographs† of such a disc before and after compression. Two such photographs are reproduced in figure 2, *a* repre-

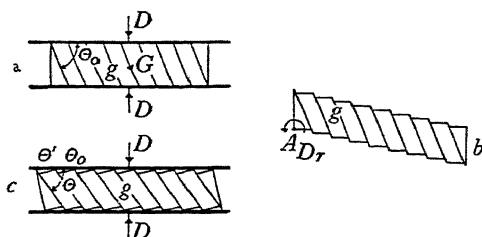


Figure 1. Change in orientation of glide lamellae during compression of a disc, cut from a single crystal.



Figure 2. X-ray rotation-photographs of an aluminium single-crystal disc: *a* before compression; *b* after compression to about 0.8 of its original thickness.

senting the undeformed crystal, *b* after compression up to  $d/d_0 =$  about 0.8. The fact that the spots on this last photograph are but little less sharp than those on figure 2 *a* indicates that the compressed disc can still be considered as being practically a "single crystal." From the relative shift of corresponding spots on both photographs, it can further be concluded that the position of the crystal lattice with regard to the surface of the disc has changed exactly in the way required by

\* G. I. Taylor and W. S. Farren, *Proc. Roy. Soc. A*, 111, 529 (1926); *A*, 116, 16 (1927).

† The discs were rotated about their normal as axis, the X-ray beam "skimming" the outermost



the glide process illustrated in figure 1, namely by a *rotation* (not a curvature) of the whole glide lamellae about the axis  $A_{Dr}$ , the line of intersection of the glide plane  $g$  with the plane of the disc.

In this "ideal" shear deformation there is no reason for any distortion of the crystal lattice. A Laue photograph of the compressed disc (figure 3 *b*) shows, however, elongated spots, thus indicating the presence of "curved" lattice regions\*. From a geometrical analysis of these Laue photographs† it can be deduced that the curvature has a definite sense, namely around an axis  $[211]$ , which lies in the glide plane (of general form  $(111)$ ) perpendicular to the glide direction (of general form  $[110]$ ); on the photograph this is shown by the fact that the spot (No. 11),

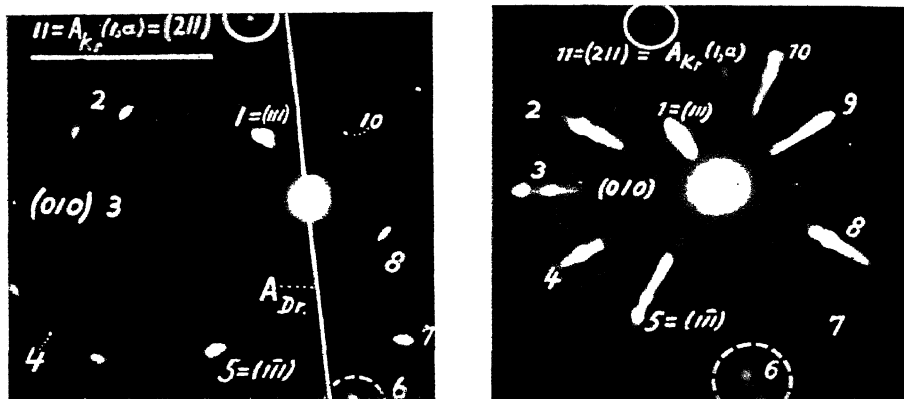


Figure 3. Laue photographs of an aluminium single-crystal disc. X-rays  $\perp$  disc-surface: *a* before compression ( $A_{Dr}$  = line of intersection of glide lamellae and disc-surface (compare figure 1)); *b* after compression to 0.86 of its original thickness.

due to reflection of the  $(211)$ -plane, which stands perpendicular to the first-mentioned axis, is practically not elongated on figure 3 *b*. It was found, further, that the degree of bending increases with the amount of shear along the glide plane.

In connexion with the homogeneous character of the deformation as a whole, the occurrence of lattice curvatures is only explicable if we assume, as has been done by Taylor and by Yamaguchi (*loc. cit.*), that they have a *local* character and are due to slip over limited regions of the slip planes. It seems probable that such "limited glide processes" are accompanied by local bendings of the glide lamellae around an axis which lies in the glide plane perpendicular to the glide direction (compare

\* The occurrence of elongated spots on Laue photographs of deformed crystals and their connexion with the glide mechanism was first studied by J. Czochochalski (*Z. f. Metallk.* 15, 60 (1923)) and A. F. Joffé and collaborators (*Z. f. Phys.* 22, 286 (1924)).

† W. G. Burgers and P. C. Louwerse, *Z. f. Phys.* 67, 605 (1931); K. Yamaguchi, *Sci. Pap. Inst. phys. chem. Res. Tokyo*, 11, 151, 223 (1929); compare also G. I. Taylor, *Trans. Far. Soc.* 24, 121 (1928); H. J. Gough, Edgar Marburg Lecture, *Am. Soc. f. Test. Mat.* 33 (11), (1933).

figure 4, which is due to Yamaguchi, *loc. cit.*), that is exactly in the sense that can be deduced from the Laue photographs by purely geometrical analysis\*.

We may perhaps get some insight into the "actual nature" of a local curvature by considering the fact that even a severely cold-worked aluminium test-piece, be it a single crystal or poly-crystalline, does not show an appreciable broadening of the Debye-Scherrer interference lines†, from which it can be concluded that the actual distortion has such a character that only a relatively small proportion of all the atoms has undergone irregular displacements from ideal lattice-positions. It

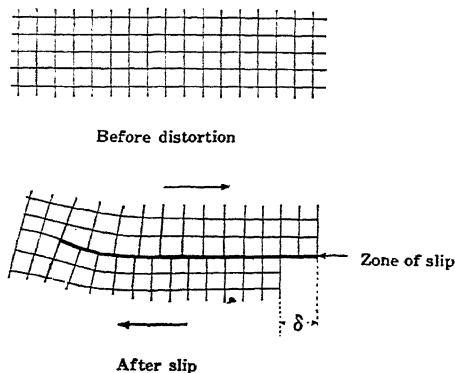


Figure 4. Schematic representation of a "local curvature" of the crystal lattice, due to slipping over a limited area. (After Yamaguchi.)

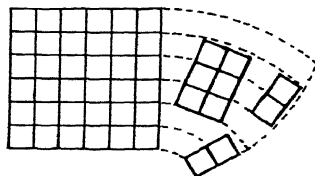


Figure 5. Schematic representation of "crystal break-up" in a "local curvature" along a glide-lamella of a deformed aluminium crystal.

seems probable, therefore, that a local curvature corresponds more or less to a "broken-up" crystal-region as shown schematically in figure 5, where the greater part of the atoms belong to undistorted or only slightly distorted lattice regions (thick lines), which are "glued together" by severely distorted regions (dashed lines)‡.

So we arrive at the conception of a uniformly distorted single crystal, in which gliding along one system of parallel glide planes has taken place, as shown schematically in figure 6 *b*, where the local curvatures are indicated by short thick

\* See also the micro-photographs in Yamaguchi's paper: *Sc. Pap.*, etc. 8, 289 (1928).

† U. Dehlinger, *Z. f. Krist.* 65, 615 (1927).

‡ Compare H. J. Gough, *loc. cit.* figure 52; see also W. G. Burgers and P. C. Louwerse, *loc. cit.* p. 613.

lines\*. Their "sense" corresponds to the rotations, which occur at the ends of a crack in an elastic material on applying shear parallel to the crack†. In case of gliding along more than one set of planes, it may be expected, and it is confirmed by analysis of the corresponding Laue photographs (for the details of which we must refer to our paper, quoted on p. 142, footnote), that "local curvatures" are formed along each of the systems of glide planes, which have taken part in the deformation process, in the way represented schematically in figure 6 *c* for two glide planes.

Now it is reasonable to assume that the "local curvatures" as a consequence of "overlapping" of atom-rows are closely related to the "dislocations" or "Versetzungen" ("Verhakungen") considered by various authors in their theories of plastic deformation, and are thus essentially connected with the hardening of the

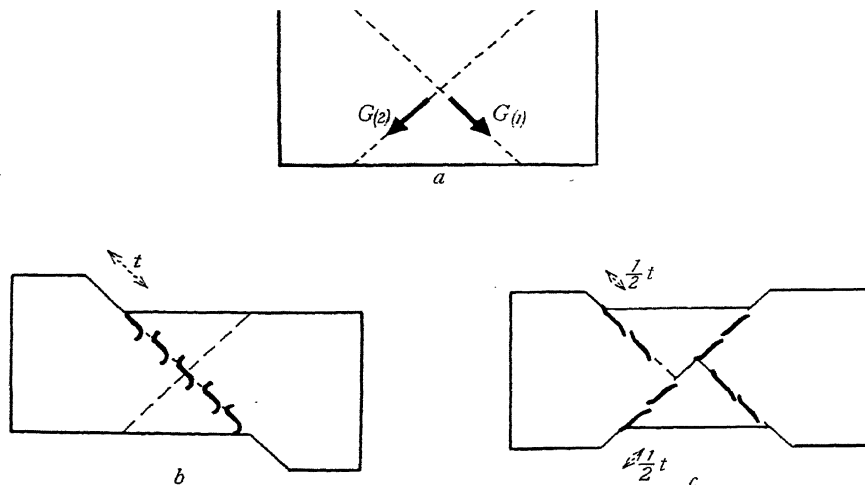


Figure 6. Schematic representation of "local curvatures" along glide planes: for a given total shear  $t$  the average degree of bending is greater in case of gliding along one (figure 6 *b*) than along two (figure 6 *c*) glide planes.

crystal against further shear. As it is known from the investigations of v. Göler, Karnop and Sachs‡ and from those of Taylor§ that the shear hardening of aluminium single crystals practically only depends on the *total amount* of shear, independent of whether this has taken place along one or along two sets of glide planes, this means that *the same shear hardening can be effected by different "systems of curvatures,"* viz. by the system of curvatures represented schematically in figure 6 *b* (one glide plane, with a "small" number of "strong" curvatures) as effectively as by that of figure 6 *c* (two glide planes, with a "large" number of "weaker" curvatures).

\* A similar schematic representation is given by H. J. Gough in his Edgar Marburg Lecture (*loc. cit.* figure 21).

† A. T. Starr, *Proc. Camb. Phil. Soc.* 24, 289 (1928).

‡ Frhr. v. Göler, R. Karnop und G. Sachs, *Z. f. Phys.* 41, 103, 116 (1927).

§ G. I. Taylor, *Proc. Roy. Soc. A*, 116, 39 (1927).

If we assume that the energy surplus (stress content) in a "strong" curvature is greater than in a "weak" curvature, we may picture in an energy diagram the two states of the deformed crystal, which relate to the *same* shear hardening, as is done schematically in figures 7 *a* and 7 *b*: in these figures the shaded areas represent the energy surplus in a "curvature"; *a* relates to gliding along one plane, *b* to gliding along two (eventually more) glide planes.

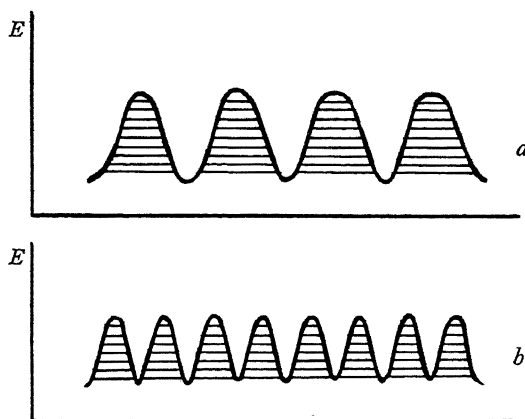


Figure 7. Schematic representations of the distribution of stress concentration in two states of a deformed crystal, relating to the same *total* shear (and thus practically the same shear hardening): *a* in case of gliding along one glide plane; *b* along two glide planes.

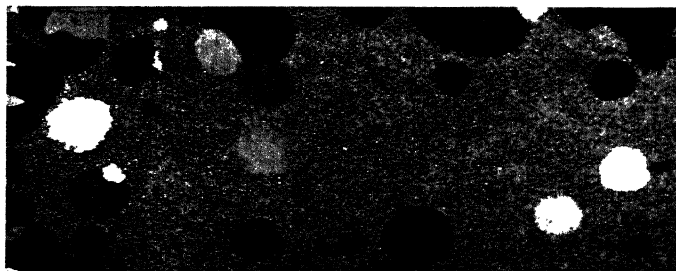


Figure 8. Recrystallization of a strained metal: the new undeformed crystals grow from nuclei.

(3) We shall now proceed to consider in what way the above picture of the "inner structure" of a "homogeneously" deformed single crystal can, at least to some extent, be confirmed by studying its recrystallization process.

Figures 8 and 9, which are due to van Arkel\*, illustrate two characteristic features of the recrystallization process in general. They both relate to fine-grained aluminium test-pieces, which have been stretched a few per cent and then heated at 600° C. for a relatively short time. Figure 8 shows that the new undeformed†

\* Compare A. E. van Arkel, *Polytechn. Weekblad*, 26, 397 (1932); *Z. f. Metallk.* 22, 217 (1930).

† Compare however p. 151.

crystals grow from definite nuclei, till they come into contact with each other. Figure 9 demonstrates how these nuclei are formed especially at those points of the deformed test-piece where the concentration of stress has been largest, as was the case in the neighbourhood of the incisions which were cut into the test-piece before stretching.

Applying these two well-known facts to the recrystallization of the homogeneously deformed aluminium single crystals, we may expect in the first place that the nuclei will be formed in the local curvatures of the glide planes. According to a point of view set forth by Dehlinger\*, we may conceive this process as consisting of a "loosening" of the severely dislocated atoms (dashed lines in figure 5) between the more or less strain-free regions (thick-drawn lines in figure 5), followed by subsequent growth of these regions. If this is actually the case, then *it must be expected that there will be a definite relationship between the orientation of the mother crystal and that of the small crystallites formed by recrystallization of a homogeneously compressed aluminium single crystal*, in the sense that the new crystallites occupy



Figure 9. On recrystallization, nuclei are especially formed in regions of stress concentration.

a definite preferred orientation, which is composed of as many different "groups" as there are glide combinations which have taken part in the deformation process, whereby the mean orientation of each individual group can be deduced from that of the original single crystal by a rotation around an axis in the glide plane considered, perpendicular to the glide direction considered. (Compare figure 4).

This conclusion could actually be confirmed in a detailed investigation† of the recrystallization of homogeneously deformed aluminium single crystals. Before showing this to be the case, figure 10 may first be given as an experimental indication of the presence of a preferred orientation in general.

It also is due to van Arkel and shows an etched aluminium plate, figure 10 *b*, which had been rolled and thereafter recrystallized. Originally, figure 10 *a*, it consisted of a few large single crystals, the boundaries of which had been marked by ink lines. Although the recrystallized plate is entirely in a finely grained state, yet the regions originally occupied by the single crystals can still be clearly discriminated, thus showing that *in each region, the new crystallites occupy some*

\* U. Dehlinger, *Metallw.* 12, 48 (1933); compare also H. G. Müller, "Zur Natur der Rekristallisationsvorgänge," *Physik. Z.* 35, 646 (1934).

† W. G. Burgers and P. C. Louwerse, *loc. cit.*; much more concisely in *Metallw.* 11, 251, 265 (1932).

*preferred orientation, differing from that of the neighbouring crystals*; this is what would be expected in connexion with the varying orientation of the original crystals, if in each of these crystals the mean orientation of the new crystallites is related in a definite way to the original orientation of the special crystal considered. The actual presence in a *homogeneously* deformed single crystal after recrystallisation, of a preferred orientation of the type mentioned above, may be clear from figures 11-13 (for details see the original papers).

They relate to the recrystallization of the disc, cut from a single crystal of aluminium, the Laue photograph of which in its undeformed state is shown in figure 3 *a*. From this photograph the positions of the cubic axes in relation to the plane of the disc were determined; they are represented by  $P_0$ ,  $Q_0$  and  $R_0$  in the stereographic projection figure 13 *b* (plane of projection parallel to plane of disc).

After careful compression (compare first footnote, page 141) up to 0.35 of its original thickness, the position of the lattice, as a consequence of rotations of the type

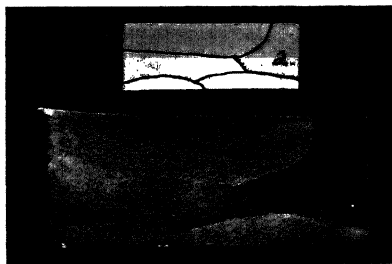


Figure 10. Recrystallization of a rolled aluminium plate, which originally (*a*) consisted of a few large crystals, the boundaries of which had been marked. In the recrystallized test-piece the regions, occupied originally by the single crystals, can still be discriminated (*b*).

represented in figure 1, had changed in such a way that (as was deduced from rotation photographs (compare figure 2)) it occupied the symmetrical "final position," represented in figure 11, in which the direction of compression is parallel to a  $[110]$  direction. In this position, which was already nearly reached after compressing up to  $d/d_0 = 0.6$ , the shear-stress conditions are equal for *four* glide combinations, viz. those operating along the octahedral planes  $g(1)$  and  $g(2)$  parallel to one or other of the two equivalent octahedral sides in each plane, for example *a* and *b* in plane  $g(2)$ . These four glide combinations can thus be expected to have taken part in the compression deformation (possibly to a different extent; see below) and to have given rise to "local curvatures" of the glide lamellae about four axes, lying in  $g(1)$  and  $g(2)$  perpendicular to the glide directions, the "sense" of these curvatures being as shown in figures 4 and 6. In figure 11 *two* of these axes, *c* and *d*, standing perpendicular to the glide directions *a* and *b* in the glide plane  $g(2)$ , are indicated, together with curved arrows, representing their "sense of rotation," as will be clear from careful consideration of the figure.

As to the positions of the cubic axes (cube poles), the resulting lattice curvature is shown in stereographic projection in figure 12 (plane of projection again parallel

to plane of disc). Figure 12 *e* shows once more the "final position" of the elementary cube in the compressed disc before recrystallization, with *one* combination of glide plane  $g$ , glide direction  $G$  and "axis of curvature"  $A_{Kr}$  specially indicated. By means of the figures 12 *a* and 12 *b*, the stereographic projection, figure 12 *c*, will be understood; here  $P$ ,  $Q$  and  $R$  represent the cube poles of the elementary cube in the compressed disc, while the three arrows indicate the positions occupied by  $P$ ,  $Q$  and  $R$  if rotated about the axis of curvature  $A_{Kr}$  (compare figure 12 *b*), which stands perpendicular to the glide direction  $G$  in the glide plane  $g$  (the "ends" of the arrows correspond to a rotation of  $50^\circ$ ). Thus

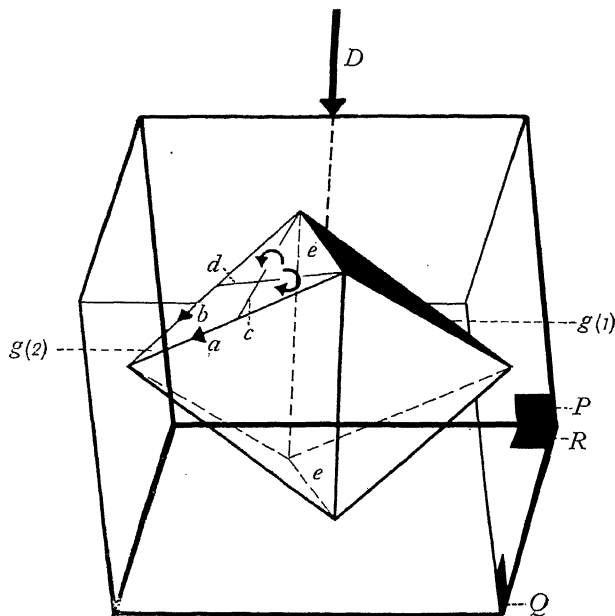


Figure 11. Final orientation of the lattice of an aluminium single crystal after continued compression: direction of pressure  $D$  parallel to a  $[110]$ -direction.

the directions of these arrows indicate, for the glide combination considered, on the one hand the "local curvatures" of the glide lamellae in the compressed disc; on the other hand they must be expected to "fix" the cube poles of the corresponding group of crystallites formed on recrystallization, in case the supposition made previously regarding the formation of crystal nuclei is correct.

Finally figure 12 *d* has been obtained by completing figure 12 *c* with regard to the three remaining glide combinations which take part in the compression deformation of the single-crystal disc, as set forth in the discussion of figure 11. Figure 12 *d* thus shows four series of curves (each drawn differently), fixing the positions of the cube poles in the *four* groups of crystallites, which can be expected to occur in a strongly compressed single crystal disc on recrystallization.

The experimental results are summarized in figure 13. Figure 13 *a* shows a

$10^\circ$  oscillation photograph of the recrystallized disc (for this purpose it was heated at  $600^\circ\text{C}$ . during a few seconds only). By means of a complete series of such "oriented" oscillation photographs the positions of the cube poles in the recrystallized disc were completely determined. The result is shown in figure 13 *b* in stereographic projection, where the different shadowing of the cube-pole regions indicate their considerable variation in "density."

Now in the first place figure 13 *b* allows the conclusion that there are actually *four*

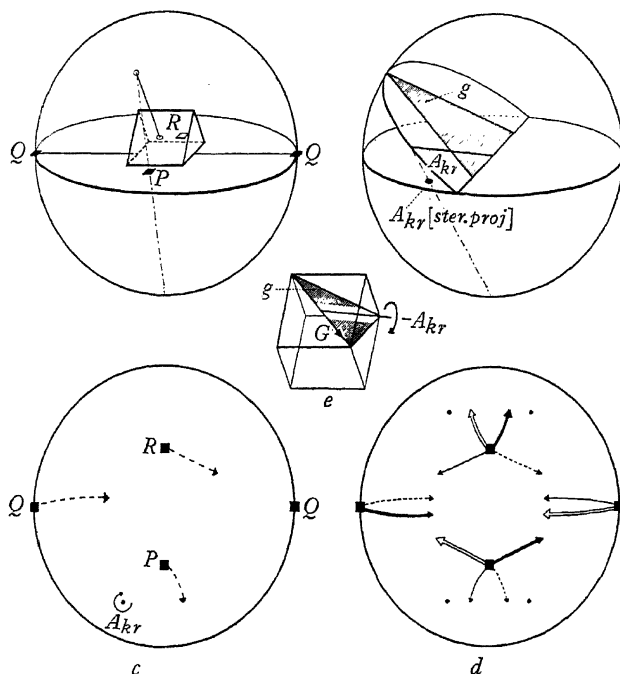


Figure 12. Representation (in stereographical projection of cube-poles) of the *fourfold* "local curvature" of glide lamellae in a severely compressed aluminium crystal about axes, which lie in the glide planes perpendicular to the glide directions (in *e* the relative position of *one* such axis  $A_{kr}$ , glide plane *g* and glide direction *G* is indicated separately).

differently oriented groups of crystallites in the recrystallized disc (each group being represented by *three* cube-pole regions at average distances of  $90^\circ$  from each other), in positions which are approximately fixed by the series of arrows of figure 12 *d*\*. The fact that the cube-pole regions show a considerable "dispersion" about the "theoretical" arrows is not surprising, as we may suppose that these

\* The projection shows only *ten* cube-pole regions instead of twelve (=four times three). This is in consequence of the fact that figure 12 *d* contains two pairs of arrows (on the left and on the right of the figure), which are so close together that the corresponding pole regions overlap in the stereographic projection of figure 13 *b*.



latter represent only average directions of curvature of the original glide lamellae: deviations will occur as a consequence of local inhomogeneities in the crystal; moreover lattice regions where different glide lamellae "cross" each other may be "curved" about more than one axis. It can be further concluded from figure 13 *b* that the orientation of the newly formed crystallites differs from that of the mother crystal by rotations of 20 to 60° about the axes  $A_{kr}$  considered. This means that conditions are favourable for crystal growth only in the severely rotated regions of the local curvature, a fact which need not be surprising, as in these regions the relative dislocation of neighbouring atoms, and thus the stress-inhomogeneity, may be largest\*.

The considerable variation in "density" of the cube-pole regions allows another conclusion to be drawn, which is of importance in connexion with what follows later (under (4)).

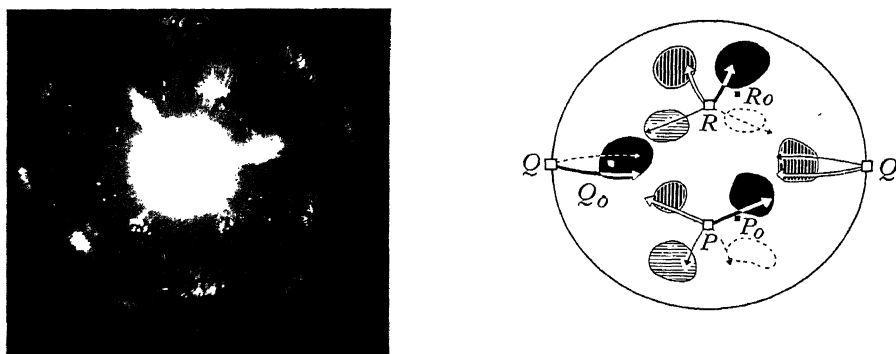


Figure 13. Recrystallization texture of a severely compressed aluminium single crystal disc after heating at 600° C. *a*, 10° oscillation-photograph, axis of oscillation in plane of disc (vertical in photograph); *b*, stereographic projection of cube-poles, and their relation to the position of the compressed crystal *before* heating: *four different groups of crystallites are present*.

From the analysis of the rotation and Laue photographs of the disc, taken after different stages of compression (and hence before recrystallization), the relative "activity" of the four glide combinations, which have brought about the change in the position of the crystal lattice from its starting position " $P_0-Q_0-R_0$ " (figure 13 *b*) into the final position " $P-Q-R$ ," could be deduced with great probability (for details see the original paper). It was found in this way that the glide combination corresponding to the thick arrows in figure 13 *b* (or 12 *d*) has been in operation from the beginning of the compression; then, after reaching a symmetrical position relative to the planes  $g(1)$  and  $g(2)$ , the glide combination corresponding to the "double arrows" also took part in the deformation process; whereas only in the last stages of the compression, when approaching the "final position" represented in figure 11, did the two remaining glide combinations (thin and

\* Compare W. G. Burgers and P. C. Louwerse, *Z. f. Phys. loc. cit.* p. 658.

dotted arrows in figure 13 *b*) come into a position, for which the shear-stress condition became equal to that of the combinations already active. From the fact, shown by figure 13 *b*, that the "density" of the cube-pole regions decreases in the same order as the "activity" of the glide combinations, it can be concluded that *for identical conditions of heating the chance to form an undeformed nucleus increases considerably with the amount of shear along a glide plane*, and thus (see under (2)) with the degree of bending of the "local curvatures."

Summing up, it can be said that *not only the individual glide processes which have taken part in the deformation but also their "relative activity" can to some extent be deduced from the recrystallization texture.*

On continued heating, a fine grained test-piece showing a definite recrystallization texture may be transformed into a few single crystals, or even only one, by subsequent growth of definite crystallites\*. Investigation† of the orientation of these large crystals has shown that, in general, their positions do *not* lie within the "regions of maximal density" of the recrystallization texture, but somewhere outside or near the "boundary" of these regions. They thus correspond with nuclei which have been formed in "local curvatures" of the glide lamellae which either in "degree" or in "direction" of bending differ from the majority. This is of interest in connexion with the concept of Dehlinger‡ referred to above, according to which even in recrystallized grains there are still "residual" distortions and stresses. It is assumed that their "amount" differs in the various grains (probably according to the "state" of that special region of the deformed lattice where a definite grain is formed), and that this difference is the "driving force" for the subsequent growth.

(4) The above-indicated analysis of deformed and recrystallized aluminium single crystals by means of X-rays confirms the schematic conception of the "inner structure" of a "homogeneously" deformed crystal as shown in figures 5 and 6, especially as to the occurrence of "local curvatures" of glide lamellae.

Although in this conception of a plastically deformed crystal the "local curvatures" are fundamentally connected both with hardening and with recrystallization power, we should *not* expect a parallelism between these two properties, in the sense that for a given crystal a definite "shear hardening" corresponds with a definite recrystallization power (this latter power being conveniently measured by the number of crystallites formed during a given heat-treatment§).

In fact, whereas it is the "total effect" of all these curvatures together, which is measured by the "hardness," it is the "distribution" of the energy surplus over the individual lattice distortion which determines the recrystallization power. This was clearly demonstrated by the analysis of the recrystallization texture of figure 13 *b*, where it was found that for definite conditions of heating, the chance of forming an undeformed nucleus increases with the amount of shear and thus with the degree of bending of a local curvature.

It is therefore clear that we may expect a *difference in recrystallization power between two crystals which have undergone the same shear hardening*, in one case (compare figures 6 *b* and 7 *a*) by shear along one glide plane, in the other case

\* A. E. van Arkel and M. G. van Bruggen, *Z. f. Phys.* 51, 520 (1928).

† W. G. Burgers and J. C. M. Basart, *ibid.* 54, 74 (1929).

‡ U. Dehlinger, *Metalw.* 12, 48 (1933).

§ It is here supposed that this number corresponds to that of the nuclei formed.

(figures 6 *c* and 7 *b*) by shear along *more than one* glide plane: in the sense that the number of nuclei will be *greater*, the *less* the number of glide planes which have taken part in the deformation process, since in this case the average bending of the "curvatures," and thus their stress content, is larger.

This is now confirmed by experiments\*, as the following examples may show.

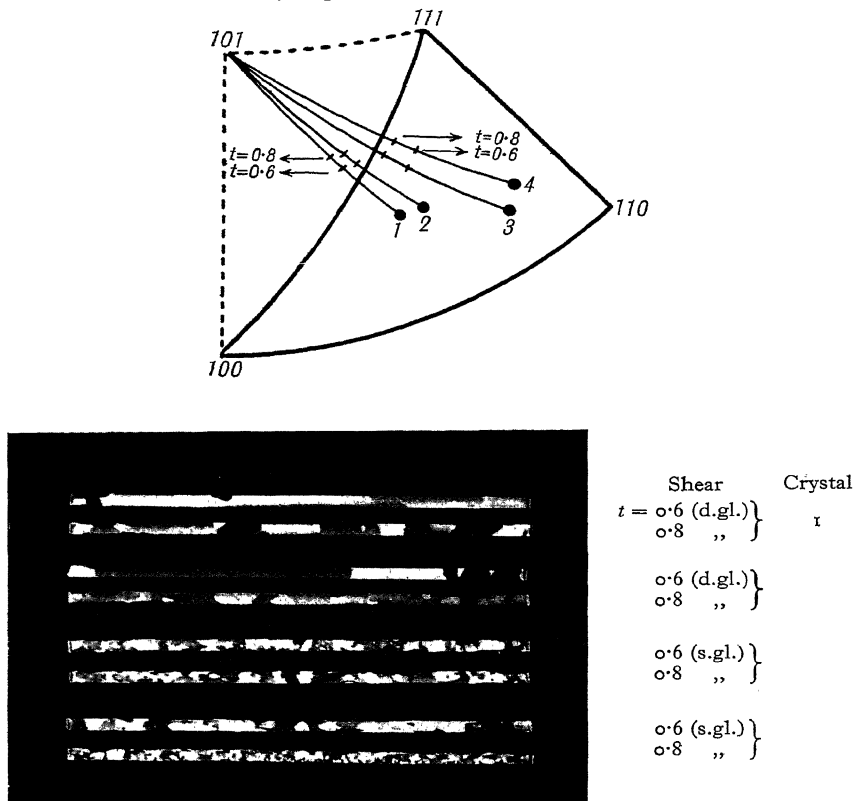


Figure 14. Difference in recrystallization power between crystals which have undergone "double gliding" (Nos. 1 and 2) and "single gliding" (Nos. 3 and 4): the number of crystals, formed for the same *total* shear  $t$ , is less in the former than in the latter: *a*, "theoretical" change in position of the lattice relative to the direction of stretching for shears  $t = 0.6$  or  $0.8$ ; *b*, recrystallized test-pieces.

Figure 14 relates to four aluminium single crystal rods, the directions of the axes of which are shown in stereographic projection. Of each crystal two pieces have been stretched so far as to correspond to shears of  $0.6$  and  $0.8$  respectively†. As is clear from the stereographic projection (figure 14 *a*), the orientation of crystals

\* W. G. Burgers and J. J. A. Ploos van Amstel, *Z. f. Phys.* **81**, 43 (1933); *Nature*, **131**, 326 (1933).

† The amount of stretching required for a definite shear can be determined for an arbitrary crystal orientation with the aid of diagrams, given in Frhr. v. Göler and G. Sachs' paper (*Z. f. Phys.* **41**, 103 (1927)).

3 and 4 was such that for both degrees of stretching, gliding took place along one glide plane only (but for the occurrence of "forbidden glidings"), whereas for crystals 1 and 2 the symmetry line  $[100]-[111]$  between two "fundamental triangles"  $[100-110-111]$  and  $[100-101-111]$  has been passed, so that "double gliding" might be expected to have occurred in these cases\*. On recrystallizing the stretched rods at  $600^\circ$  for 15 min., the number of crystals (figure 14 *b*) formed in these last rods, in which double gliding has taken place, is much less than in rods 3 and 4, where only one set of glide planes has taken part in the deformation process, in accordance with the view set forth above.

The same effect can be shown in a much more striking way by the following experiment. It is a well-known fact that on stretching an aluminium single crystal, not only the "theoretical" glide plane for which the component of shear stress is maximal, but also so-called "forbidden glidings" take part in the glide process to a greater or lesser extent. If we assume the probability of gliding in a definite glide plane to be proportional to the shear stress along this plane, we may predict for what direction of stretching the probability of the occurrence of multiple gliding is largest and smallest respectively, by calculating† the *average* of the shear stresses along all twelve possible glide combinations for different directions of stretching. As this quantity, expressed in terms of the applied tensile stress as unity, varies from 0.27 for the  $[100]$  direction to 0.14 for the  $[110]$  and  $[111]$  directions, we find that the probability of multiple gliding is largest for the  $[100]$  direction (for this direction the ratio  $\frac{\text{shear stress}}{\text{tensile stress}}$  has a *high* value (0.41) for eight of the twelve possible glide combinations) and smallest for the  $[110]$  and  $[111]$  directions.

We may thus expect a difference in recrystallization power for aluminium crystals of varying orientation, stretched over the same total shear, in the sense that the number of crystallites formed on heating will be larger, the nearer the crystal axis lies to the line  $[110]-[111]$ . This is confirmed by figure 15 *b*, where five crystal rods are shown, the orientations of the axes of which are again represented in stereographic projection in figure 15 *a*.

The maximal difference in recrystallization power may be expected to exist for aluminium crystals stretched along  $[100]$  and along  $[110]$ , in the sense that the former gives rise to the formation of a smaller number of crystals than the latter. This is now confirmed by experiment in a striking way, as is clear from figure 16, which shows four pieces of an aluminium single crystal, *two* (figure 16 *a'*) with the length direction parallel to  $[100]$  and *two* (figure 16 *b'*) with their direction parallel to  $[110]$ . On stretching all these crystal pieces 10 per cent, that is, as calculation shows, practically to the same total amount of shear, their hardening proved to be practically the same; Laue photographs showed, however, that the spots (figure 16 *a*) of the crystal stretched parallel to  $[100]$  have practically remained unaltered, whereas those (figure 16 *b*) of the crystal stretched parallel to  $[110]$  have been elongated, thus

\* G. I. Taylor and C. F. Elam, *Proc. Roy. Soc. A*, 108, 28 (1925); Frhr. v. Göler and G. Sachs, *Z. f. Phys.* 41, 103 (1927).

† Compare W. Boas and E. Schmid, *Z. f. techn. Phys.* 12, 71 (1931).



(5) Thus we finally come to the conclusion that a definite shear hardening may be connected with different states of lattice distortions, i.e. schematically speaking, the "co-operation" of a large number of "weak" curvatures or a small number of "strong" curvatures. The recrystallization power is attributed to the "distribution" of stress content over the individual curvatures; it is thus conceivable that the first state gives rise to the formation of a smaller number of crystallites than the latter state.

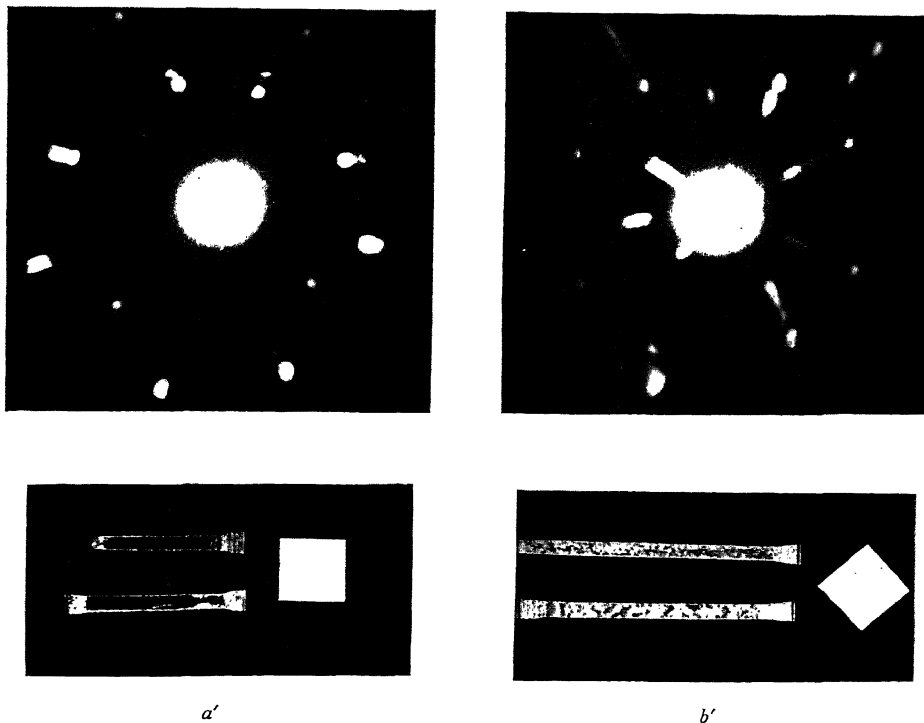


Figure 16. Difference in distortion and in recrystallization power on stretching an aluminium single crystal to *practically the same* shear hardening: *a*, *a'*, (nearly) parallel to a  $[100]$ -direction; *b*, *b'*, (nearly) parallel to a  $[110]$ -direction.

If now we stretch a test-piece consisting of a number of differently oriented crystals, we may expect that the recrystallization power of the individual crystals will be different, as some have undergone "simple" and others "complicated" shear, thus giving rise to different systems of "lattice curvatures" within them. That this expectation comes true is clearly shown\* by figures 17, 18: the three crystallites I, II and III, marked in figure 17 *a*, after stretching the whole test-piece about 10 per cent, gave rise to the Laue photographs in figure 18 *a*, *b* and *c* respectively. After heating the test-piece at  $600^{\circ}$  (figure 17 *b*) several new crystallites

\* W. G. Burgers, *Metallw.* 11, 265 (1932).

were formed in II, and *none* in I, in accordance with the fact that the Laue spots in photographs 18 *a, b* indicate the presence of "stronger curvatures" (corresponding to a "simpler" glide process) in II than in I (III represents an intermediate state).

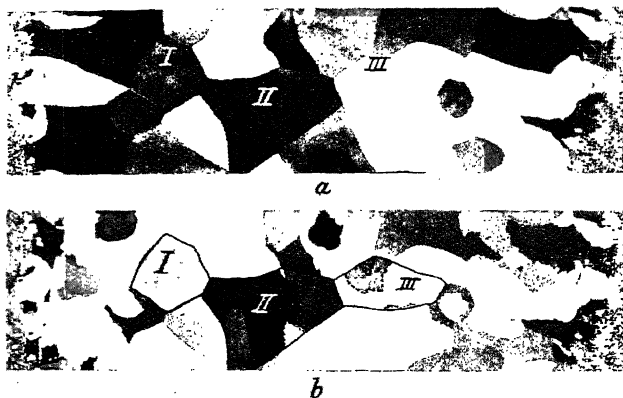


Figure 17. Difference in recrystallization power between *various* crystals of a polycrystalline test-piece: *a*, original state; *b*, after 10 per cent stretching and subsequent heating at 600° C.: the number of crystallites formed in the crystals I, II and III is quite different (none in I, several in II, a few in III).

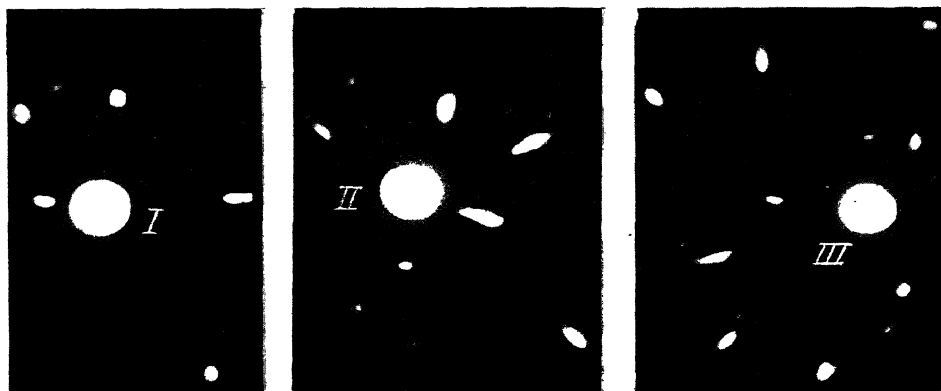


Figure 18. Laue photographs of crystals I, II and III in the *stretched* aluminium plate of figure 17 *a* *before* recrystallization.

This difference in recrystallization power of the individual crystallites of a polycrystalline test-piece, in connexion with the extreme recrystallization power of crystals stretched along [110], seems to us to give an explanation of the experimental fact, observed by several investigators\*, that large aluminium crystals, grown by recrystallization of strained

\* C. F. Elam, *Phil. Mag.* 50, 517 (1925); E. Schiebold and G. Sachs, *Z. f. Krist.* 63, 34 (1926). For further references see note \*, p. 152.

polycrystalline test-pieces, seem to favour a position in which a [110] direction is parallel to the direction of stretching: it seems probable that, on stretching a polycrystalline aggregate, a crystal grain of this special orientation will exhibit an extreme recrystallization power and serve as nucleus for the single crystal formed on heating.

The above may perhaps help us to understand the experiments of van Arkel and van Bruggen\*, who found that aluminium test-pieces of rather variable crystal size, after stretching to the same load per mm<sup>2</sup>, on heating give rise to the formation of an equal number of crystallites: their test-pieces consisted in all cases of a fairly large number of crystallites, so that in a given test-piece crystallites were present which, if we neglect the influence of the glide distortion at their boundaries, had undergone simple, as well as others which had undergone complicated shear; thus the number of crystallites formed on heating was probably the average for all crystal orientations for the given shear applied †, and the differences observed by us for single crystals need not occur in their experiments. It is, however, difficult to discuss these experiments in detail, as, of course, the hardening caused by the glide distortions at the boundaries of the crystallites plays an important part in this case.

That, however, the parallelism between hardening and recrystallization power, as shown in this case, is more accidental than fundamental and due to the special conditions of the experiment, is clear from experiments with crystals under flexural and torsional stress, as have been performed by Czochochalski, Sachs, Beck and Polanyi, and van Arkel and van Bruggen. For details we must refer to the original papers‡. Here only one experiment may be mentioned, described by Beck and Polanyi§, which clearly demonstrates the fundamental *non*-parallelism between the two properties mentioned. An aluminium single-crystal rod was bent through a certain angle and then restraughtened over half its length. Ball-hardness tests showed that the restraughtened part was "harder" than the bent part; on recrystallization, however, crystallites grew in this latter "weaker" part, whereas they were not formed in the "harder" straight part of the crystal rod.

In connexion with the foregoing, we may say that regarding the "distribution" of stress concentration, the bent and the restraughtened part of the crystal rod can be discriminated by such schematic figures as those given in figures 7*a* and 7*b* respectively. Thus we attribute the decrease of recrystallization power on restraughtening, in agreement with Polanyi, to a decrease of stress content in the "curvatures" formed during the foregoing bending, whereby the increase of the hardening can be accounted for by the formation of new ("small") curvatures (and consequent lattice distortions) as a result of the working of other glide planes on restraughtening||.

\* A. E. van Arkel and M. G. van Bruggen, *Z. f. Phys.* **42**, 795 (1927).

† On account of the high degree of symmetry of aluminium, a given stretch corresponds approximately to a given *total* shear for all crystal orientations: see v. Göler and Sachs, *loc. cit.*

‡ See for references, and for a more detailed discussion of these experiments, W. G. Burgers, *Z. f. Phys.* **81**, 43 (1933).

§ P. Beck and M. Polanyi, *Naturwiss.* **19**, 505 (1931); *Z. f. Elektroch.* **37**, 521 (1931).

|| On further bending in the same direction, the average curvature can increase again and with it the recrystallization power: compare A. E. van Arkel and M. G. van Bruggen, *Z. f. Phys.* **80**, 804 (1933) for analogous experiments with crystals under torsional stress.



## APPENDIX\*

(6) "*Transformation-hardening.*" Before concluding this paper, a few words may be added regarding a type of recrystallization process, which is essentially different from that considered so far. It occurs, at least in several cases (carbon-steel, brass, cobalt, zirconium), on transition of one phase (modification) of a metal or alloy into

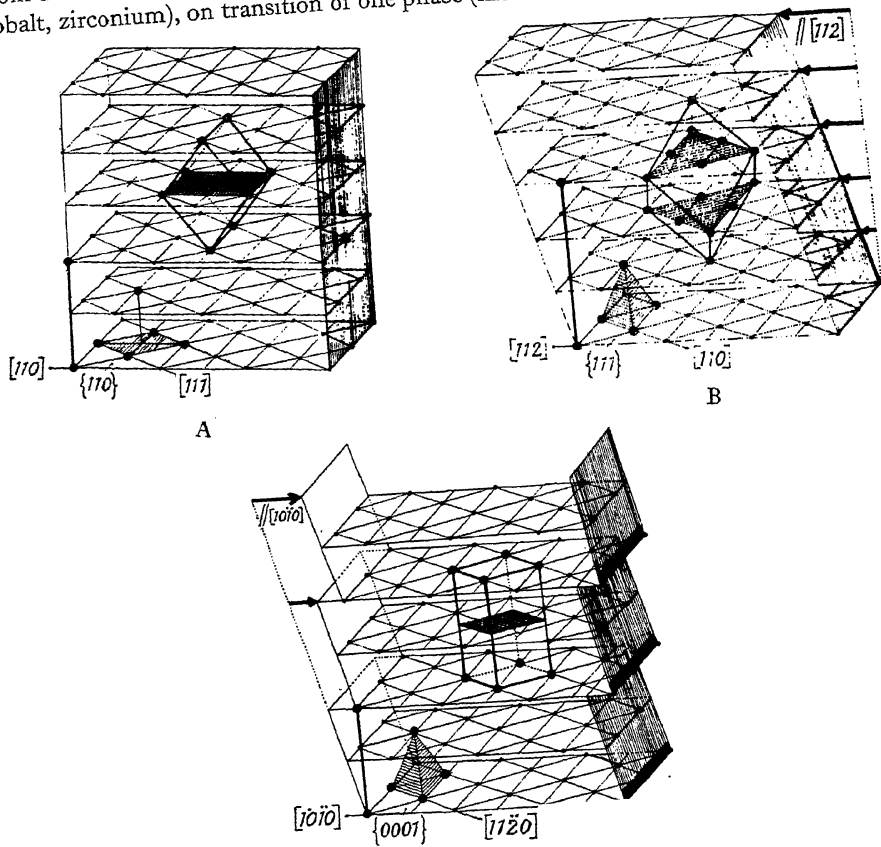


Figure 19. Schematic illustration of the shearing operations, which can transform a body-centred lattice A, via an intermediate face-centred lattice B, into a lattice with atoms in positions corresponding to those of the hexagonal close-packed lattice C†.

another, and can be described as a homogeneous deformation of the initial crystal lattice, consisting of one or more simple shears parallel to definite crystallographic

\* See for references concerning a large number of papers by several investigators, dealing with the questions raised in this appendix, W. G. Burgers and F. M. Jacobs, "On the process of transition of the cubic body-centred modification into the hexagonal close-packed modification of zirconium," *Physica*, 1, 561 (1934).

† The actual transformation of a cubic body-centred lattice via a cubic face-centred lattice into a truly hexagonal close-packed lattice requires an additional shear operation, together with special dilations and contractions of the lattice, which are not illustrated by figure 19.

planes and directions, combined with (in general small) dilatations or contractions. Figure 19 may serve as an illustration: it shows the way in which for example a sequence of two shear operations may transform a definite body-centred lattice A via an intermediate face-centred lattice B into a lattice C with atoms in similar positions to those occurring in the hexagonal close-packed lattice; the shear plane corresponding in the various lattices to a  $\{110\}$ , a  $\{111\}$  and a  $\{0001\}$  plane respectively\*.

It is clear that the shear operations lead to the existence of a definite crystallographic relation between the orientation of the crystals of the newly formed phase and those of the original phase. Thus, for example, a single crystal of the cubic body-centred modification of zirconium, while passing over into the hexagonal close-packed modification at about  $870^{\circ}\text{C}$ ., gives rise to a limited number (maximally 12) of orientations of the hexagonal lattice; these being such that in each of them the  $\{0001\}$  plane and a  $[11\bar{2}0]$  direction are parallel respectively to a  $\{110\}$  plane and a  $[111]$  direction of the cubic lattice. It is actually from the existence of such a crystallographic relation that the "mechanism" of the process can be deduced, at least to some extent.

In some cases, however, an experimental indication of the occurrence of a "homogeneous" process is obtained, if, after transition of an  $\alpha$  phase into a  $\beta$  phase and back again, the *original* orientation of the  $\alpha$  crystal is obtained again: this will occur if the same shear plane (s) and direction (s) have been active in both transition processes. An example of this is shown in figure 20, which again relates to the transition of cubic into hexagonal zirconium and *vice versa*.

In connexion with the subject of the present paper, it is, moreover, of interest to point to a characteristic feature of such a "homogeneous" transition process, viz. that smaller or larger regions of the original crystal lattice are "coherent" with regard to the transition, so that nowhere within them are the initial and the final states of the metal simultaneously present.

This may lead to a remarkable difference between this process and that occurring on recrystallization of a strained metal with regard to their *influence on the hardness* (and eventually other physical properties, as electrical resistance, magnetic hardness) of the metal. Whereas in a strained test-piece the growth of nuclei (see figure 8) gives rise to the formation of practically stress-free crystallites†, and thus to an "annealing" of the test-piece, *the transformation process, on the contrary, may cause it to become harder.*

In fact, as a consequence of the presence of different "equivalent" shear planes in a crystal lattice, or (in the case of a polycrystalline test-piece) of differently oriented crystallites, the directions of the transformation shears and contractions (or dilatations) need not be the same in the whole test-piece. It is, therefore, conceivable that internal stresses and distortions may be created by "shear interference" between neighbouring lattice regions, which themselves are coherent with regard to the transformation.

\* See p. 158, footnote †.

† Compare however p. 151 (small print).

Such an effect may give rise to a "hardening" of the test-piece: it was actually observed in a rod consisting of zirconium crystals, if by rapid cooling the transition point was passed as quickly as possible, in order to prevent release of tension of the

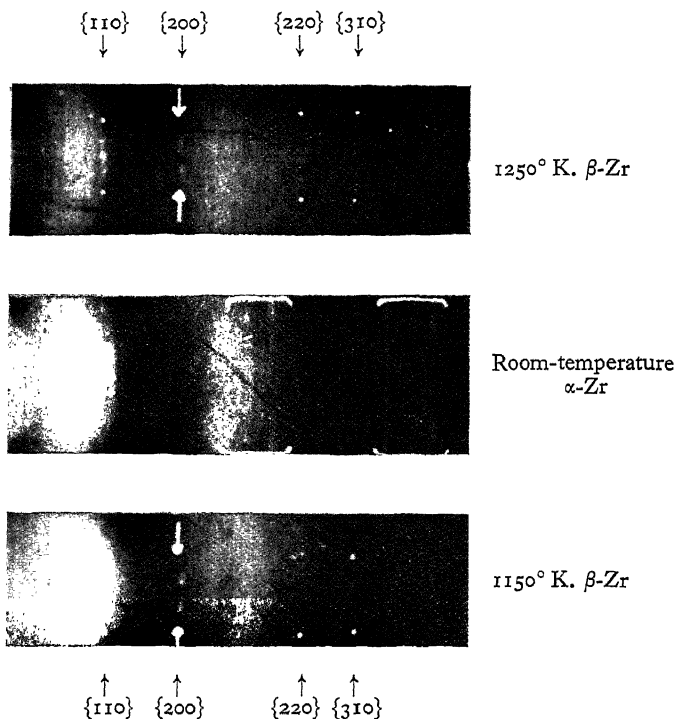


Figure 20. X-ray rotation photographs\* of a definite part of a zirconium wire at different temperatures. Photographs *a* and *c* show practically the same arrangement of spots (see especially the identical positions of the  $\{200\}$ -reflections); in this case, therefore, a cubic  $\beta$ -crystallite regains its original orientation after the transition of the hexagonal  $\alpha$ -phase (photograph *b*) and back again.

\* Unfortunately these photographs have been damaged rather badly by scratches. Moreover they show a strong diffuse scattering, due to the Lindemann glass surrounding the wire.

stresses introduced by the transformation process. By heating such "hardened" crystals at a temperature not too much below the transition point, they can be made weak. An analogous behaviour was observed by Wassermann† in nickel-iron wires, which were subjected to repeated transitions from the cubic face-centred into the cubic body-centred phase.

† G. Wassermann, *Arch. f. das Eisenhüttenw.* 6, 347 (1933).

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# ON PLASTICITY, CRYSTALLOGRAPHIC AND NON-CRYSTALLOGRAPHIC

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**ABSTRACT.** The paper is largely devoted to summarizing experimental data on crystal plasticity. It is pointed out that with regard to elasticity, Cauchy's relations are in general obeyed by ionic, but not by metallic, crystals.

The behaviour of crystals with regard to plasticity is then considered, first with reference to slip and then to mechanical twinning. As regards the former, which is marked particularly by the fact that it occurs in directions and along planes which are definitely marked out in the crystal lattice, it is pointed out that yielding shows an abrupt onset, and commences at a definite critical shear stress. This quantity is tabulated for a number of crystals, and its temperature variation shown graphically. It is pointed out that, just as the yield point can be expressed by this single constant, so the stress-strain curve can be expressed in a single curve, the hardening curve. In this, the shear strength of the slip system concerned is plotted as a function of the shear. This curve gives at once the hardening due to any degree of shear.

As regards twinning, the available knowledge is less quantitative. The effect of temperature on it is less marked than on slip, and like the latter process, it leads to strengthening of the crystal.

The final section of the paper deals with those types of plasticity which show no definite relation to the net-planes of the lattice. Among these processes are creep and a remarkable plasticity during phase-change of specimens under load.

IN the theory of the solid state, the investigations which would be expected to give in the most direct manner a measure of lattice forces, namely those on the strength of crystals, still present a difficult problem. The object of this paper will be to bring forward in a very condensed form some experimental data on crystal deformation, at a conference where help in the explanation of the results may confidently be expected.

## 1. THE ELASTICITY OF CRYSTALS; CAUCHY'S RELATIONS

Even in the elastic deformation of metals a remarkable divergence from theory is encountered, which was noticed very early<sup>(1, 2)</sup>. The equations expressing the generalized Hooke's law for triclinic crystals involve 21 constants. This number is reduced to 15 if no account is taken of the interaction between the component simple lattices. That is, six new relations are obtained, identical with those obtained by Cauchy in 1828. These six equations are:  $c_{23} = c_{44}$ ,  $c_{56} = c_{14}$ ,  $c_{64} = c_{21}$ ,  $c_{31} = c_{55}$ ,  $c_{12} = c_{66}$  and  $c_{45} = c_{36}$ \*. According to Born's theory, these relations

\*  $c_{ik}$  and  $s_{ik}$  are elastic constants (Voigt's notation).

should be valid if each element of the crystal is a centre of symmetry. Since this latter property cannot be destroyed by elastic displacements, mutual interaction of the component lattices is already excluded by the assumed structure of the crystal. Table 1 gives the values of the elastic constants of several materials. It will be seen

Table 1. Validity of the Cauchy relations

$$c_{12} = c_{44} \text{ valid}$$

Crystal	$c_{12}$ $10^{11}$ Dyn./cm <sup>2</sup>	$c_{44}$ $10^{11}$ Dyn./cm <sup>2</sup>
NaCl	1.37	1.28
NaBr	1.31	1.33
KCl	0.64	0.65
KBr	0.58	0.62
KI	0.43	0.42
Cu	12.3	7.52
Ag	8.97	4.36
Au	15.7	4.36
Al	6.22	2.84
$\alpha$ -Fe	14.1	11.6
W	19.8	15.1

$$c_{12} = c_{44} \text{ not valid}$$

Crystal	$c_{12}$ $10^{11}$ Dyn./cm <sup>2</sup>	$c_{44}$ $10^{11}$ Dyn./cm <sup>2</sup>
CaF <sub>2</sub>	4.48	3.38
NaClO <sub>3</sub>	2.10	1.20
FeS <sub>2</sub> (Pyrites)	4.74	10.55

$$c_{11} = 3c_{12}; c_{13} = c_{44} \text{ not valid}$$

Crystal	$c_{11}$ $10^{11}$ Dyn./cm <sup>2</sup>	$3c_{12}$ $10^{11}$ Dyn./cm <sup>2</sup>	$c_{13}$ $10^{11}$ Dyn./cm <sup>2</sup>	$c_{44}$ $10^{11}$ Dyn./cm <sup>2</sup>
Mg	5.65	6.96	1.81	1.68
Zn	16.3	7.65	5.08	3.79
Cd	12.1	14.4	4.42	1.85

that whilst polar (ionic) crystals show the relations which would be expected from their structures, the metallic crystals exhibit a gross lack of agreement. Since, however, there can hardly be any doubt as to the stability of these lattices, the only available explanation is that the second assumption, concerning the non-interaction of the component lattices, is not justified, and therefore the easily detachable electrons of the metals must be considered as independent constituents of the lattice.

## 2. TYPICAL CASES OF CRYSTAL PLASTICITY

Whilst as regards elastic behaviour, polar crystals agree with theory and only metallic crystals show a decided discrepancy, yet the plastic behaviour of both types differs most markedly from that indicated by theory.

## (a) Slip

Slip is in the first place characterized by the strictly crystallographic selection of the slip elements, slip planes and direction. In general the preferred direction of slip is the line of greatest density in the lattice (in the case of polar crystals that most thickly beset with metallic ions), and the planes of slip are particularly densely packed planes of the lattice. Table 2 shows that the mechanical condition of maximum elastic shear can only play a subordinate part, if any, in the selection of the slip elements. As the examples in the table show, the actual slip systems (corresponding to those values printed in black type in the table) are not by any means always characterized by the maximum specific shear (elastic shear produced by unit shear stress).

Table 2. Slip systems and corresponding specific shears\*:  $\gamma = \tau/G$ 

## (a) Cubic crystals:

Slip parallel to		Specific shear ( $\tau/G$ )	NaCl	KI	CaF <sub>2</sub>	Al	Cu	Au
Plane	Direction							
		(10 <sup>-13</sup> cm <sup>2</sup> /Dyn.)						
(001)	} [110]	$s_{44}$	78.0	238	29.6	35.2	13.3	22.9
(110)		$2(s_{11}-s_{12})$	56.0	89.2	16.8	43.4	42.6	66.1
(111)		$\frac{4}{3}(s_{11}-s_{12}) + \frac{1}{3}s_{44}$	63.3	138.7	21.1	40.6	32.8	51.7

## (b) Hexagonal crystals:

Slip parallel to		Specific shear ( $\tau/G$ )	Mg	Zn	Cd
Plane	Direction				
		(10 <sup>-13</sup> cm <sup>2</sup> /Dyn.)			
(0001)	} [112̄0]	$s_{44}$	59.5	26.4	54.0
(101̄0)		$2(s_{11}-s_{12})$	60.0	14.6	27.6
(0001)		$s_{44}$	59.5	26.4	54.0

\* For notation and elastic constants see reference<sup>(3)</sup>.

Dynamically, slip is usually characterized by its very abrupt commencement in crystals at extraordinarily low stresses. After a small amount of purely elastic deformation and then of slight plastic deformation with accompanying rapid increase of stress, there follows a very large amount of deformation, sometimes accompanied even by a decrease in load. Figure 1 shows the well-defined nature of the "yield point" of crystals as thus defined, the example chosen being some creep-rate curves for cadmium crystals. The distinctness of the yield is often increased by the fact that at first it occurs locally and gradually extends over the whole crystal (see figure 2).

A quantitative law for the value of the yield point, which has been verified in all the cases hitherto investigated, asserts that the commencement of yielding is associated with the attainment of a definite *critical shear stress*<sup>(5)</sup>. A summary of the values of these critical stresses, determining the ease with which slip occurs in various materials, is given in table 3. The shear stress for slip systems other than the principal one is only known in the case of tin crystals. In this case there are four crystallographically distinct slip systems which have only slightly

different shear strengths; it thus follows that the possibility of slip is not entirely determined by the density of packing<sup>(6)</sup>. In general, however, the preference for the principal slip system is very marked, as may be seen from the variations in orientation over which it remains operative.

Figure 3 shows some data on the relation between critical shear stress and temperature in hexagonal metallic crystals. It will be seen that the shear strength

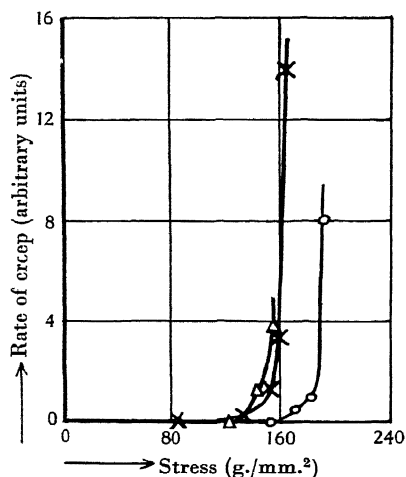


Figure 1. Distinctness of yield in Cd crystals.



Figure 2. Commencement of local extension in a Cd crystal<sup>(4)</sup>.

of slip systems is only influenced to a small degree by the temperature. For example, the shear strength of the basal plane slip system of cadmium crystals is only increased about fourfold by decreasing the temperature from almost the melting point to  $20^{\circ}$  abs. Further cooling to  $1^{\circ}$  abs. has practically no effect<sup>(7)</sup>. Near the melting point, metals show a region of practically constant critical shear stress\*. Similarly small effects of temperature on the commencement of plasticity have been observed in the case of the cubic metals aluminium<sup>(8)</sup> and tungsten<sup>(9)</sup>. In order to investigate the plasticity of rock salt crystals at low temperatures, they have been subjected to torsion<sup>(9)</sup>. The results were very similar to those found in

\* The effect of the variation with temperature of the solubility of impurities cannot yet be assessed separately.

metal crystals. The proportional limit in torsion, i.e. the stress at which deviation from Hooke's law first occurs, for the dodecahedral slip system, is found<sup>(9)</sup> to be only 6 to 7 times as high at 20° abs. as at room temperature (see figure 4). Increasing

Table 3. Critical shear stresses of the principal slip systems of crystals (at 20° C.)

Crystal	Total impurities (parts per thousand)	Slip system		Critical stress g/mm <sup>2</sup>
		Plane	Direction	
Cu	< 1	{ (111)	[110]	100
Ag	0.1			60
Au	0.1			92
Ni	2.0			580
Mg	0.5	{ (0001)	[1120]	83
Zn	0.4			94
Cd	0.04			58
β-Sn	0.1	(100) (110)	{ [001]	189
				133
Bi	~ 1	(111)	[101]	221
NaCl	0.3	{ (110)	[110]	75
KCl	0.16			50
KBr	0.3			80
KI	0.2			70

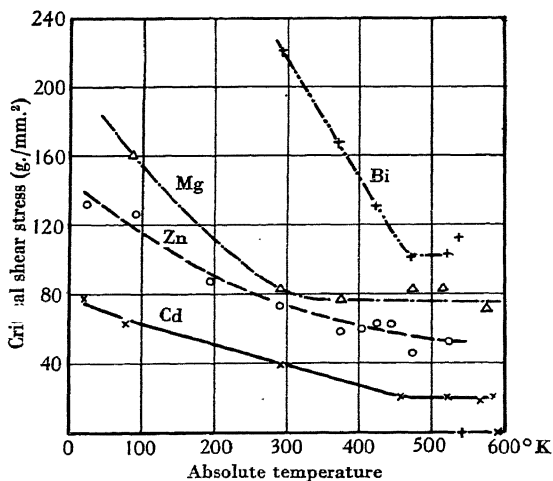


Figure 3. Relation between critical shear stress and temperature in metallic crystals<sup>(3)</sup>.

the temperature above 20° C. leads at first to an increase in shear strength, as had already been observed in tensile tests<sup>(10)</sup>. The fact that at higher temperatures new slip systems are sometimes observed (e.g. in Al, Mg, NaCl, BaSO<sub>4</sub>) shows also that the alteration in shear strength is not uniform on all planes of the lattice.



Just as the yield point, which depends on the position of the slip elements, can be expressed by a single constant, the critical shear stress, so the course of the stress-strain curve, which depends on the orientation, can be expressed in a single

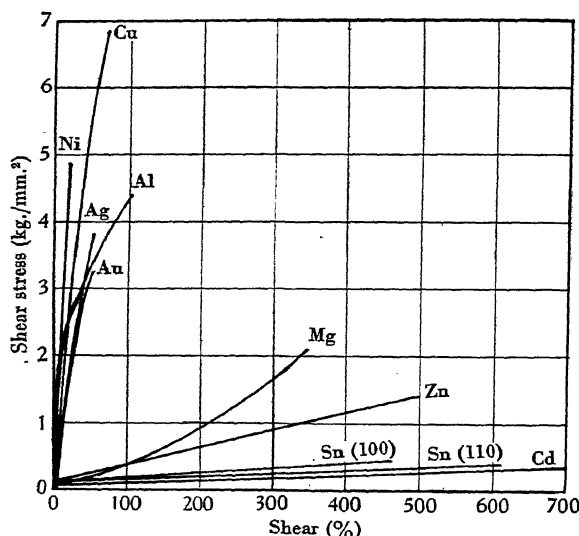
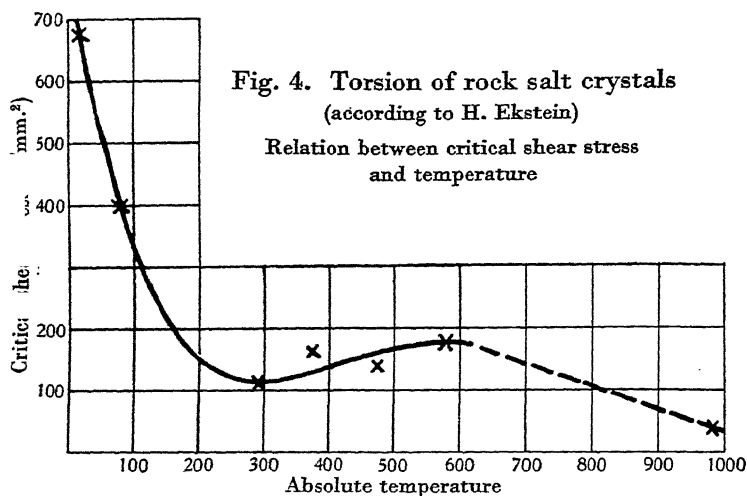


Figure 5. Hardening curves for metallic crystals.

curve, the "hardening curve" (Verfestigungskurve)<sup>(11)</sup>. In this the shear strength of the operative slip-system is plotted as a function of the shear (relative displacement of two slip planes at unit distance apart); from it the hardening (increase in strength) of the crystal can be read directly. Figure 5 shows the form of the

hardening curve for crystals of all the pure metals so far investigated. The basal plane of hexagonal crystals (also the slip systems of tin) shows a much lower resistance to slip than the octahedral slip systems of the face-centred cubic metals. This cannot be regarded as due entirely to the difference in melting points, as the cases of aluminium and magnesium show. The very rough representation in figure 6 of the methods of two close packing of spheres may perhaps help to make plausible the very different behaviour of crystals of these two types (see also<sup>(12)</sup>). The upper half of the figure shows spheres piled in the two different ways; in the hexagonal close packing, the spheres in the third row (not shown in the figure) come vertically above those in the first row, whilst in the cubic close packing only the fourth row comes exactly over the first. In the lower half of the figure, sections are shown representing these planes for which the spheres, which for this purpose are taken

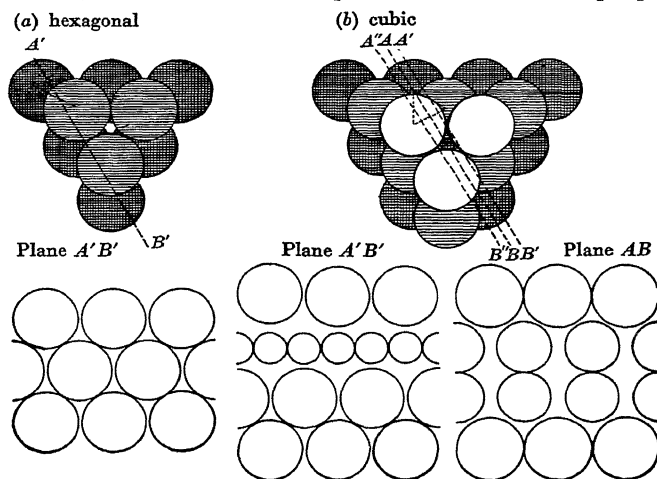


Figure 6. Slip in hexagonal and cubic close packed crystals.

to represent atoms, undergo slip\*. The behaviour of hexagonal crystals is seen to be much simpler than that of cubic crystals.

In polar crystals also, deformation is accompanied by considerable strengthening of the crystal. Quantitative hardening curves have however not yet been obtained. This is due to the fact that, in the crystals of the rock-salt type to which most attention has so far been devoted, the crystallographic identity of the slip direction with the normal to the slip plane causes duplex slip to occur even at the commencement of the normal tensile test<sup>(13)</sup>. Crystals of the caesium chloride type (slip plane  $(110)$ , direction  $[001]$ ) should form suitable material for such an investigation.

The effect of temperature on the hardening curve is very slight at high or low temperatures, but very considerable in the middle range. Here there is a transition from the steep curve at low temperatures, indicating considerable hardening, to the flat curve obtained at high temperatures<sup>(14)</sup>.

\* The section  $A''B''$  is obtained from  $A'B'$  by exchange of the two middle rows.

What conditions govern the *cessation of slip* cannot yet be stated with certainty. The type of phenomenon following slip (mechanical twinning, cleavage, or the development of a tic or of a crack) certainly plays an important part. With regard to the very illuminating condition put forward as a result of alternating bending tests on steels<sup>(15)</sup> and static torsion and compression tests on copper<sup>(16)</sup>, namely, that failure occurs when the material has absorbed a certain amount of internal energy, it may be said that corresponding test results on single crystals are not available. Tests on zinc crystals, which have shown<sup>(17)</sup> that prior deformation in alternating torsion increases very considerably the energy absorbed to fracture in tension, do not necessarily disprove this energy hypothesis, as the heat evolved was not measured.

### (b) *Mechanical twinning*

Our knowledge of the second typical crystallographic deformation phenomenon, the mechanical development of twins, is still practically limited to the crystallographic nature of the twinning elements. This type of deformation, which consists in portions of the crystal taking up positions symmetrical to the original lattice about the twinning element, extends in general in a way which is macroscopically discontinuous. Frequently the transition to the twinned state occurs so rapidly that the deformation is accompanied by loud reports. The stresses necessary to cause twinning are of the same low order as those necessary for slip. No quantitative dynamical condition for the initiation of twinning is yet known. This is due in the first place to the very marked sensitivity of twin formation to the presence of inhomogeneity; for this reason mechanical twinning always occurs over a more or less wide variation in stress. In the second place, twinning is often accompanied and disturbed by slip.

The effect of temperature on twinning appears to be still smaller than that on slip, as is shown by the failure of twinning at high temperatures in zinc and cadmium, and by the occurrence of twinning in preference to slip at low temperatures in  $\alpha$ -iron.

Twinning, like slip, leads to strengthening of the crystal. For instance, the shear strengths on the basal plane of twin lamellae of zinc and cadmium crystals at room temperature are increased about twofold<sup>(18)</sup> and threefold<sup>(4)</sup> respectively. In agreement with this, twin lamellae form extremely favourable centres for recrystallization (see figure 7). For example, annealing at temperatures over 145° C. for 1 min. always produces recrystallization in twin lamellae of strained cadmium crystals, whilst in the twin-free areas a temperature of at least 240° C. is necessary.

In considering the theoretical aspects of these two mechanisms of deformation, it may be remarked that it is now well established that *the observed low strengths on the slip and twinning planes cannot be regarded as the strength of the lattice\**. Variations in the modulus of rigidity have never been observed at stresses below the onset of plastic deformation; the elastic shear at the yield point or at the commencement of twinning is of the order of  $10^{-4}$  and not about 0.5 of that necessary for the overcoming of the shear strength of the lattice. Opinions are

\* The same may be said of the tensile strength of crystals (not dealt with here).

still widely divergent as to the reasons for this premature failure in crystals and for the strengthening which accompanies deformation. *Lack of structural and of thermal homogeneity* have been regarded as responsible, both separately and in combination. In general, recent opinion in the case of slip (see particularly<sup>(19, 20, 21)</sup>) is that the slip does not occur simultaneously throughout the whole cross-section of the crystal, but only locally in small regions, afterwards spreading through the whole

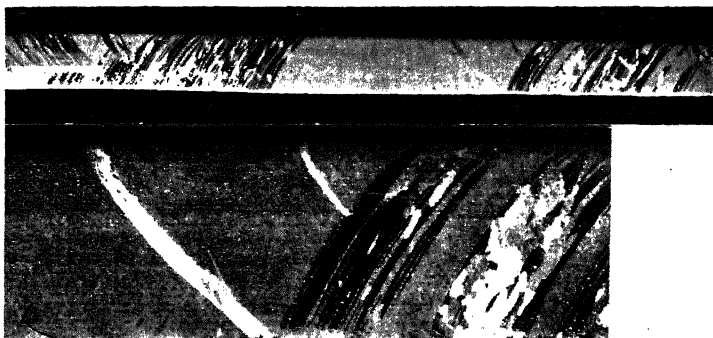


Figure 7. Recrystallization of strained Cd crystal commencing from twin lamellae.

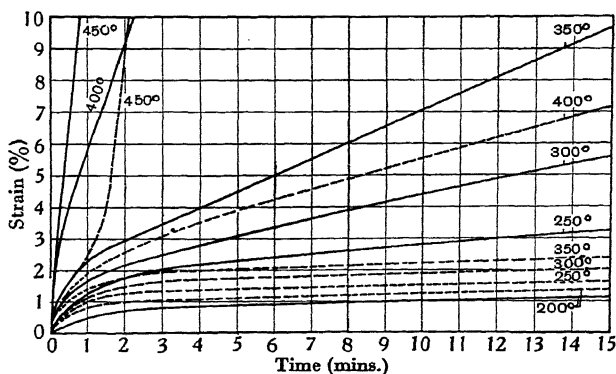


Figure 8. Effect of temperature on creep curves of hard and soft copper wire<sup>(24)</sup>.  
Stress 1.6 kg./mm<sup>2</sup>

— hard      - - - soft.

crystal. That similar diffusion phenomena, depending on the slip system and the induced stresses, may also be taken as a model of twin formation is, however, hardly likely. In this case, the attainment of stable equilibrium necessitates that all the atoms in the neighbourhood of a particular atom shall change their positions simultaneously.

### 3. NON-CRYSTALLOGRAPHIC PLASTICITY

A special type of plasticity, which probably cannot be regarded as due to crystallographic slip motion, is shown by crystalline materials when sudden changes

of position occur (e.g. in recrystallization or phase change). Under the influence of external stresses that type of position-change will naturally be preferred (as in the case of plasticity in amorphous bodies) which results in a reduction of stress or plastic deformation, according to the applied load. In this way a recrystallized and therefore soft, annealed material may, above the recrystallization temperature, be stronger and more resistant than the hardened material, in which sudden changes of position take place on heating<sup>(22)</sup>. Tests on spirals of tungsten<sup>(23)</sup> and on wires of aluminium and copper<sup>(24)</sup> do in fact show considerable creep when recrystallization occurs. As an example, figure 8 shows creep curves at high temperatures for hard and soft (annealed at 600° C.) copper wires; in all cases the hard, recrystallizing wire creeps more than the soft annealed wire. Similar results have also been found in the investigation of the "creep strength" of iron, nickel and various alloys of these metals at elevated temperatures<sup>(25)</sup>. The significance of this fact in practice is self-evident.

Detailed investigation of the phase change has been carried out in an iron-nickel alloy (30 per cent Ni)<sup>(26)</sup>. If by cooling, the change from the (face-centred cubic)  $\gamma$ -phase to the (body-centred)  $\alpha$ -phase occurred while the wire was under stress, it was accompanied by extensions up to 10 per cent. In this case also the change of position of the atoms is associated with a mechanically weak state.

## REFERENCES

- (1) M. BORN. *Probleme der Atomdynamik*, p. 136 (Berlin, 1926).
- (2) P. P. EWALD. In Müller-Pouillet, *Lehrb. d. Physik*, 1/2, 11th ed. p. 936.
- (3) E. SCHMID and W. BOAS. *Kristallplastizität* (Berlin, 1935); see the bibliography given in this book.
- (4) W. BOAS and E. SCHMID. *Z. f. Phys.* **54**, 16 (1929).
- (5) E. SCHMID. *Proc. Int. Congr. Appl. Mech.* Delft 1924, p. 342.
- (6) I. OBINATA and E. SCHMID. *Z. f. Phys.* **82**, 224 (1933).
- (7) W. MEISSNER, M. POLANYI and E. SCHMID. *Z. f. Phys.* **66**, 477 (1930).
- (8) W. BOAS and E. SCHMID. *Z. f. Phys.* **71**, 703 (1931).
- (9) H. EKSTEIN. Unpublished.
- (10) W. THEILE. *Z. f. Phys.* **75**, 763 (1932).
- (11) R. KARNOP and G. SACHS. *Z. f. Phys.* **41**, 116 (1927); E. SCHMID, *ibid.* **40**, 54 (1926).
- (12) H. G. SOSSINKA, B. SCHMIDT and F. SAUERWALD. *Z. f. Phys.* **85**, 761 (1933).
- (13) E. SCHMID and O. VAUPEL. *Z. f. Phys.* **56**, 308 (1929).
- (14) M. POLANYI and E. SCHMID. *Naturw.* **17**, 301 (1929); W. BOAS and E. SCHMID, *Z. f. Phys.* **61**, 767 (1930); see also (7).
- (15) A. ONO. *Proc. 3rd Int. Congr. Appl. Mech.* Stockholm, **2**, 305 (1930).
- (16) G. I. TAYLOR and H. QUINNEY. *Proc. R.S.* **143**, 9 (1934).
- (17) E. SCHMID. *Z. f. Metkde*, **20**, 69 (1928).
- (18) E. SCHMID and G. WASSERMANN. *Z. f. Phys.* **48**, 370 (1928).
- (19) G. I. TAYLOR. *Proc. R.S.* **145**, 362, 388, 405 (1934).
- (20) E. OROWAN. *Z. f. Phys.* **89**, 605, 614, 634 (1934).
- (21) M. POLANYI. *Z. f. Phys.* **89**, 660 (1934).
- (22) R. BECKER. *Z. f. techn. Phys.* **7**, 547 (1926).
- (23) F. KOREF. *Z. f. techn. Phys.* **7**, 544 (1926).
- (24) E. SCHMID and G. WASSERMANN. *Z. f. Metkde*, **23**, 242 (1931).
- (25) W. ROHN. *Z. f. Metkde*, **24**, 127 (1932).
- (26) G. WASSERMANN. *Arch. f. Eisenhüttenwesen*, **8**, 347 (1932-33).

## DISCUSSION

Dr H. J. GOUGH. The papers to which we have listened deal with the discrepancy that apparently exists between the theoretical strengths of solids and their observed strengths as determined under *static* tests to destruction. Yet if we choose suitable *cyclic* stress conditions, solids—and particularly metals—can be fractured under repetitions of a stress which is only about 50 per cent of the usual value of the practical strength. This type of failure—which for want of a better term is called “fatigue” failure—possesses features which render it of special interest in the present connexion, quite apart from its importance in engineering construction. A striking characteristic is that even the most ductile metals fracture in an apparently brittle manner; no appreciable change of general shape occurs, but fracture results from a spreading crack. Detailed study of fatigue cracking has established that this failure originates in local regions: it is found that, in a piece of metal consisting of hundreds of millions of crystals, cracking commences in a very few isolated crystals and spreads from these centres: it has also been established that these centres represent crystals which have suffered considerable plastic deformation by slip. The extension of this study of fatigue to single crystals of ductile metals, such as aluminium, copper, silver, zinc, iron, etc., has revealed that the process of failure is exactly similar to that of crystalline aggregates, while the use of microscopical and X-ray methods has enabled the characteristics of failure to be correlated with the crystalline structure. In every case investigated, cracking has originated on the site of slip bands which represented slipping, under cyclic shearing forces, on definite crystallographic planes and in definite crystallographic directions. But of the available slip planes, slip actually occurs on a few only, while the slip bands do not extend right across the crystal but are of short length: the pitch, or distance apart, of the slip bands decreases with increasing range of applied shear stress. Now, although fatigue cracks always originate on the site of slip bands, yet cracking is not inseparably associated with slip, for, provided the applied range of stress has less than a certain limiting value, slip ceases, hardening is effected and fracture does *not* result. When this limiting value is exceeded, however, cracking can be observed to commence, leading to complete fracture. *Cracking is, therefore, a local effect and is a consequence of previous plastic deformation.* The changes in the nature of the X-ray reflexions obtained from crystals plastically deformed under cyclic stresses suggest that the crystal structure thereby becomes distorted or broken up in a manner which is equivalent to rotations of parts of the crystal about an axis contained by the slip plane and perpendicular to the slip direction, and it is reasonable to suppose that in this manner stresses are set up of an altogether different order of intensity from the average stress estimated merely from the externally applied load and the total dimensions of the specimen. *Thus, the actual stresses causing rupture may conceivably approximate to what are sometimes assumed to be the theoretical strengths of metals.* Experiments are now in hand to determine if a quantitative estimate can be obtained by the aid of X-ray methods of precision for the intensity of the strains induced in these local regions.

It will be seen that the above tentative conclusions derived from the study of the fatigue characteristics of metals bear many general points of resemblance to those reached by other researchers dealing with the rupture strength of solids under static forces. It is interesting to note that entirely different and independent methods of attack upon what appear to be two distinct problems converge in a very satisfactory manner upon the basic problem of cohesion.

The question now arises: Must the initial low resistance of metals to plastic deformation be ascribed to an imperfect structure, requiring the assumption of intrinsic flaws, loose structures or mosaic structures? If the strengths of metals are to be calculated from the forces necessary to separate atom entirely from atom, then such assumptions may, perhaps, become necessary and permissible. But metals deform by shear and, as far as I am aware, no estimate has yet been made of their resistance to sliding. At the present time, it appears to me that existing knowledge of the cohesive forces of the "metallic" types of combination is much too incomplete to warrant definite statements concerning the theoretical strengths of metals. A closely associated and highly important aspect of the strength of metals, of which too little is known, is that of the process of strain hardening: crystal break-up, lattice distortion, and preferred orientation all fail to offer an adequate explanation. Changes in the distribution of the free electrons have been suggested as the primary cause of the hardening of metals, and if this proves to be the case, fundamental knowledge of the true nature of slip may become available. In any case, the non-satisfaction of the Cauchy relations seems to indicate quite clearly that the inter-atomic forces are not purely central forces depending only on the atoms themselves.

Thus, until quite recently, a fair statement of the position would have been that the observed characteristics of the deformation of metals appeared to be *consistent* with the theories of Intrinsic Flaws *or* of Loose Structure *or* of Mosaic Structure, but that none of these was sufficiently definite to enable us to construct a *quantitative* theory to account for the finer and more important characteristics of the deformation and fracture of ductile metals. In my opinion, however, the recent theory of Prof. Taylor has profoundly altered our outlook on the whole problem. By assuming the presence of random dislocations, probably due to thermal oscillations, and applying the methods of the theory of elasticity, he has constructed a quantitative theory which leads to conclusions regarding slip, strain hardening, the local strains resulting from slip, the elastic limit, and the influence of the test temperature upon these and other characteristics of plastic deformation, which are in marked general agreement with the results of observation. The fact that *some* crystals give shear stress-strain relations which do not conform to the parabolic form predicted by the theory is not, I suggest, of great importance at the present stage of development of the theory. One of the most interesting aspects of Prof. Taylor's theory is that it requires, as an essential, the presence within the crystal of some type of "interference structure" to limit the path of the migrating dislocations: he has shown that the dimensions of this structure are of the same order as that of the "secondary" structure of whose existence so much circumstantial evidence of a variety of types has been obtained.

Lest I be misunderstood, I firmly believe that we should preserve entirely open minds on all theories, however attractive, which assume that the existence of imperfect structures is required to explain the characteristics of solids, *until after the nature of their cohesive forces has been clearly determined and shown to demand the existence of such imperfections*. At the present time, however, no such fundamental foundation exists, and until this has been provided by the mathematical physicists, it is extremely helpful to build up tentative theories with which to compare the results of observation and experiment. In this direction Prof. Taylor has made a notable contribution to our knowledge of the subject, and I venture to express the hope that he will continue to explore the implications of his theory.

Prof. E. N. da C. ANDRADE. During the last few years a number of investigations have been carried out in my laboratory on single crystals of metals, with special reference to the purity of the metal, in particular with cadmium and mercury. The work on cadmium was begun in conjunction with Dr Chalmers, and continued in conjunction with Dr Roscoe, while Mr Hutchings and Mr Greenland have co-operated in the work on mercury. Mercury was chosen since not only can it be prepared free from metallic contamination to a very high degree<sup>(1)</sup> (impurities not exceeding 1 part in  $10^8$ ), but it is also free from dust and dissolved gases, both of which have been mentioned as causes likely to lead to departures from the perfect lattice. Perhaps I may be allowed to mention that I prepared single crystals of mercury, and of other metals, early in 1914<sup>(2)</sup>.

Single crystals of cadmium, lead and bismuth have been prepared by the use of a narrow furnace which travels along relative to the wire: with a suitable relation between the temperature gradient and the velocity of travel, single crystal wires can be produced which give much more constant results than, e.g., those prepared by the Czochralski method, used by Boas and Schmid<sup>(3)</sup>. With crystals of cadmium prepared by this method the law of critical shear stress, referred to by Dr Schmid, has been confirmed to a closer degree than hitherto. The resolved shear stress does not depend upon the rate at which the crystal is grown, so long as it is a single crystal: with the Czochralski crystals this is not the case.

Dr Roscoe<sup>(4)</sup> has made a remarkable observation on the effect of surface in cadmium crystals. With a superficial layer of oxide one or two molecules thick, the critical shear stress may be as high as twice the value obtained with a clean surface. If the oxide is dissolved off half a single crystal wire, we may have considerably different critical shear stresses in two parts of the same wire; other experiments show that it does not matter whether the oxide film is formed during the growth of the crystal, or subsequently. Frequent reference has been made to-day to the effect of treatment of the surface on the strength of rock salt crystals, but this appears to be the first time that a surface influence has been recorded with metals. No doubt with a clean surface the initial slip which takes place at the critical shear stress is due to minute cracks in the surface, much as has been described by Dr Orowan for rock salt, and the effect of the oxide layer is to round off and strengthen the sharp edges at which the stress is high.



The cadmium used by us contained initially some 0.11 per cent zinc and 0.03 per cent lead as impurities. Further purification reduced both the critical shear stress and the plastic hardening, measured by the slope of curve of resolved shear stress against shear (see E. Schmid, figure 5). With our purest cadmium at room temperature the critical shear stress was 13.7 g./mm<sup>2</sup>. With our purest mercury at -50° C. it was 9.3 g./mm<sup>2</sup>, while for very pure zinc Hanson<sup>(5)</sup> has recently found 9.1 g./mm<sup>2</sup>. All the values are of a lower order than those given by Dr Schmid, being not much more than a tenth of his. There is an indication that the value may be about the same for all metals. We propose to investigate the change of critical shear stress with temperature for very pure metals, and also to carry out experiments with a metal deliberately contaminated with small amounts of a foreign metal, in order to extrapolate to absolute purity. It is important to know if the critical stress tends to a finite value.

With cadmium, Dr Roscoe and I have found that the two impurities present, zinc and lead, have each a different effect. Small quantities of lead increase the critical shear stress, while small quantities of zinc increase the plastic hardening. While lead crystallizes in cubic form, zinc, like the cadmium, is hexagonal. It is possible that the thermal diffusion of lead atoms takes place less readily than that of zinc atoms, which, from the work of W. L. Bragg and E. J. Williams<sup>(6)</sup> on the behaviour of alloys in which both metals belong to the same type of lattice, would be expected to move about freely to the positions of minimum potential energy. The sharp corners of internal flaws appear from the type of consideration put forward by Kossel and Stranski to be such positions. Lead atoms may be able to diffuse to the surface because of the greater freedom of thermal movement near the surface, in a tangential direction, of planes intersecting the surface.

Mercury<sup>(13)</sup> at about -50° C. shows well-marked glide, the glide planes being particularly sharp, as can be seen from figures 1 and 2, which represent respectively an early and a later stage of glide in the same crystal. An addition of 0.5 per cent of silver raises the critical shear stress considerably, but does not affect the spacing of the glide planes. These, however, lose their sharpness, and appear diffuse, as seen in figure 3. This suggests that the impurities tend to diffuse to the glide planes. There are many points of interest about mercury. It crystallizes on the rhombohedral system, and doubt has been expressed<sup>(7)</sup> as to whether glide, as distinct from twinning, can be obtained from crystals of this system. We have found that mercury glides on the rhombohedral faces, the glide direction being the short diagonal, and no sign of glide on the hexagonal base has ever been obtained by us, although this has been suspected of being the glide plane for tellurium<sup>(8)</sup>, which is also rhombohedral. With mercury the rhombohedral face and the hexagonal base are planes packed equally closely, within the experimental error of the angle determination, but the rhombohedral face contains a much more closely packed line, which is possibly the deciding factor. No other case seems to be known where these conditions prevail. Mercury twins on the plane through the long diagonals of the opposite faces, figure 4 being given as an example of the appearance of a twinning boundary. In all cases where the projection of the glide direction coincided approximately

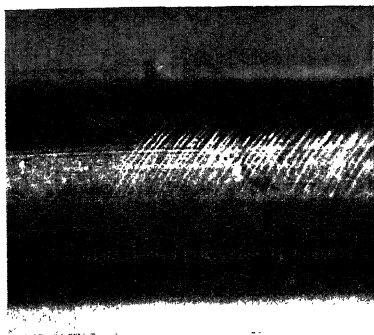


Figure 1. Glide planes on pure mercury:  
early stage.

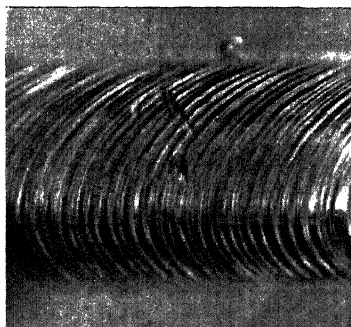


Figure 2. Glide planes on pure mercury:  
late stage.

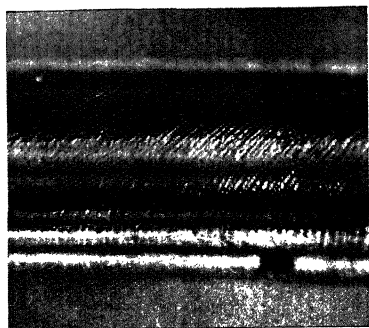


Figure 3. Glide planes on mercury  
containing 0.5 % silver.

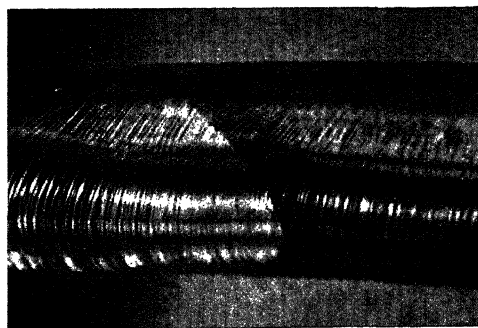


Figure 4. Twinning boundary on mercury at  
 $-50^{\circ}\text{C}$ .



Figure 5. Twinning bands on mercury  
at  $-180^{\circ}\text{C}$ .

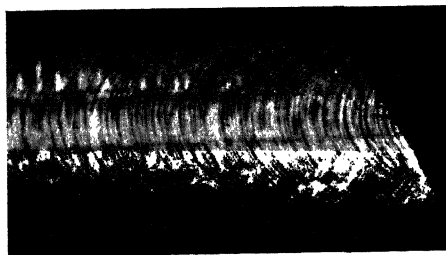


Figure 6. Glide planes on bismuth  
at  $264^{\circ}\text{C}$ .

with the direction of pull (wire axis), twinning took place when the twinning plane made an angle of  $45^\circ$  with the wire axis. In this case both the old and the new glide planes are equally favourably placed for glide. How general this criterion may be is a matter for further investigation.

Mr Greenland and I have found that mercury at  $-180^\circ$  twins much more readily

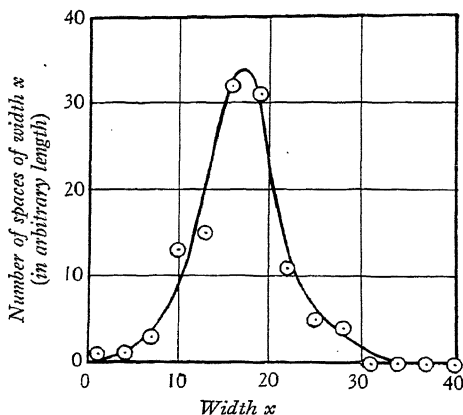


Figure 7. Distribution of spacing of glide planes in lead.

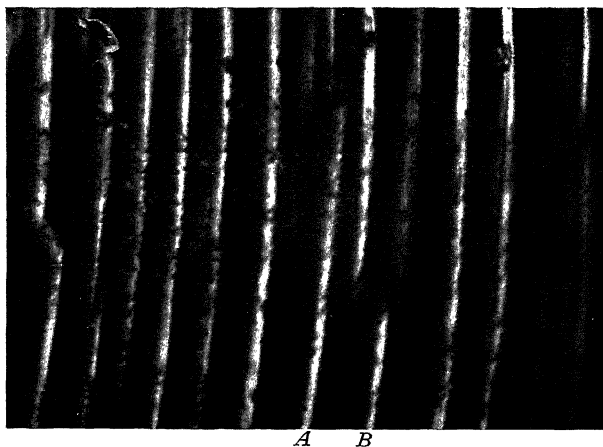


Figure 8. Slip lines in lead ( $\times 800$ ).

and extensively than at  $-50^\circ$ , with the characteristic “cry” (figure 5). This suggested that with rhombohedral metals, at any rate, glide takes place more readily at high temperature. Dr Roscoe and I therefore tried to produce glide in bismuth at a temperature  $5^\circ$  below the melting point, and procured a beautiful system of slip bands (figure 6), whereas at atmospheric temperature we found extensive twinning and no ordinary glide, in agreement with Gough and Cox<sup>(9)</sup>. This behaviour is in

direct contradiction to the examples quoted by Dr Schmid, of twinning, in preference to slip, at high temperature in zinc and cadmium, and shows how difficult it is to generalize in this field.

We have made measurements on the spacing of the glide planes. With mercury and lead the initial system of glide planes, when once developed, remains without addition for a considerable extension, although ultimately new bands appear between the old ones. The spacing of the planes is not constant, but has the ordinary chance distribution about a most probable value, as exemplified by lead (figure 7), where the most probable value is  $4.2 \times 10^{-4}$  cm.\* Figure 8 shows the slip lines for lead, at a magnification of 850, and it is interesting to note how incomplete slip bands running from top to bottom terminate close to the ends of others running from bottom to top. This is strongly reminiscent of G. I. Taylor's theory of plastic deformation<sup>(10)</sup> by the migration of faults, or centres of dislocation, under the influence of stress. The slip bands run slightly past one another, and where there are two bands terminating near the end of a band running from the opposite direction, the more distant of the two runs a little farther past (see figure 8, lines at *A* and *B*). It is to be further noted that the more widely spaced bands are complete. All this agrees with Taylor's calculation that the stress required to make one of two opposed bands run past the other is inversely as the distance between the bands. Taylor also calculates that the furthest distance by which two bands can overlap without running on completely is equal to the distance between them, which also appears to be roughly confirmed. The average spacing, too, is of the order demanded by Taylor's theory, viz. a few times  $10^{-4}$  cm.

The spacing in lead is a real feature of the crystal, and has been found to be independent of the diameter of the wire, temperature of stretch ( $0^\circ$  and  $100^\circ$ ), rate of stretch (varied by a factor of 3000) and amount of extension, which suggests that it is due to a feature initially present in the metal, and not to a development of periodic anomalies by the action of the stress itself.

General conclusions from the experiments quoted are that critical shear stress is determined by surface imperfections, while plastic flow and plastic hardening are determined by internal flaws, variously called faults, crevices, or "Lockerstellen," to which metallic impurities segregate. It is suggested that, to comply with energy requirements, these impurities in all cases go to the sharp corners of both surface and internal cracks, where they can adapt themselves to the lattice and where they exercise a strengthening effect.

Finally, as regards the rotation of crystallites, discussed by Burgers, Chalmers and I<sup>(11)</sup> have shown by measurements of electrical resistance, and Gibbs and Ram Lal<sup>(12)</sup>, working in my laboratory, have shown by X-ray methods, that, when a polycrystalline wire of cadmium or of tin is extended, a rotation of the axes of the crystallites takes place. These metals show a hardening. On the other hand, with glass, which, as Joffé points out, shows no influence of plastic flow on mechanical strength, Ram Lal has found, by X-ray methods, that there is no rotation of the crystallites. I showed many years ago that polycrystalline wires flowing plastically

\* Measurements of Dr Roscoe.

under constant stress eventually reach a stage where there is no hardening, i.e. where flow linear with time takes place. The X-ray experiments and electrical resistance experiments just quoted show that at this stage there is no progressive rotation of the crystallites. It is possible, then, that the intercrystalline boundaries can act in a way somewhat similar to that suggested by Burgers for the "cracks" in a single crystal, and produce rotation when there is a shear component along them.

## REFERENCES

- (1) E. G. A. HULETT, *Phys. Rev.* **33**, 307 (1911).
- (2) *Phil. Mag.* **27**, 869 (1914).
- (3) *Z. f. Phys.* **54**, 16 (1929).
- (4) *Nature*, **133**, 912 (1934).
- (5) *Phys. Rev.* **45**, 324 (1934).
- (6) *Proc. Roy. Soc.* **145**, 699 (1934).
- (7) E. G. H. J. GOUGH, Marburg Lecture, *Amer. Soc. for Testing Materials*, **33**, Part II (1933), and H. J. GOUGH and H. L. COX, *J. Inst. Metals*, **48**, 227 (1932).
- (8) E. SCHMID and G. WASSERMANN, *Z. f. Phys.* **46**, 653 (1928).
- (9) *Proc. Roy. Soc.* **145**, 362 (1934).
- (10) *J. Inst. Metals*, **48**, 227 (1932).
- (11) *Proc. Roy. Soc.* **138**, 348 (1932).
- (12) *Phil. Mag.* **18**, 949 (1934).
- (13) *Proc. Roy. Soc.* **148**, 120 (1935).

Dr W. F. BERG. Prof. Andrade mentioned the problem of the plasticity of bismuth crystals. I want to report a few results obtained on this material. Bismuth crystals are shown by Georgieff and Schmid\* to exhibit plastic deformation by slip. Later, Gough and Cox† and others were quite unable to find slip on bismuth crystals under similar stress conditions.

In my opinion this difference is due to the different methods of making the crystals. Georgieff and Schmid made their crystals under atmospheric pressure, whereas Gough and Cox made them *in vacuo*. I have applied both methods and the results of both papers were confirmed. Rough mechanical tests were made and the following results were obtained and published a short time ago‡:

(1) Crystals made in air show slip in tensile tests. Figure 1 shows clear slip lines on such a crystal. To show that the crystal has become a flat ribbon, part of it has been tilted 90°.

(2) On crystals made *in vacuo* no traces of slip could be detected in tensile tests.

(3) These crystals, however, exhibit slip bands in compression tests, where bigger stresses can be applied than in tensile tests. Figure 2 shows slip bands in the original crystal and in several mechanical twins, as described in *Nature*‡.

(4) Crystals made *in vacuo* are deformed by slip in tensile tests at higher temperatures (250 C.°). Figure 3 shows the two pieces of a crystal which was pulled apart. One part has been turned through 90° to show the typical deformation. There are two systems of slip lines, one of them due to slip in the {111} plane and

\* *Z. f. Phys.* **36**, 759 (1926).

† *J. Inst. Metals*, **48**, 227 (1932).

‡ *Nature*, **133**, 831 and **134**, 143 (1934).



Figure 1.



Figure 2.



Figure 3.

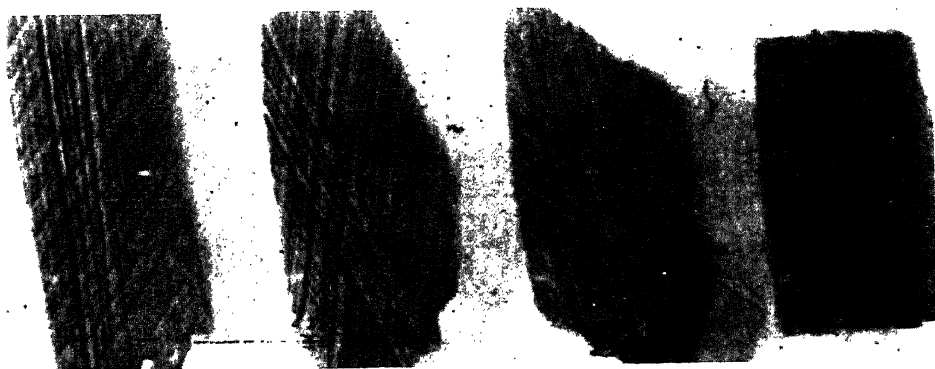


Figure 4.

the other either due to slip in the  $\{11\bar{1}\}$  plane or to slip in the  $\{111\}$  plane of a twinned part of the crystal.

According to a personal communication from Dr Gough (3) is confirmed by his latest experiments and it is interesting to hear that Prof. Andrade's experiments in which very pure material was used confirm (4) above.

The explanation why the crystals made in air are soft seems to be that they contain some of the gas which was used for cooling. Such crystals were heated *in vacuo* and a fair amount of gas came out. The amount was estimated by measuring the pressure obtained. There were about  $3 \times 10^{-4}$  molecules of gas per atom of bismuth in these crystals. This figure, however, still needs further confirmation. Besides this difference in the surroundings of the growing crystals, the other conditions (temperature gradient, velocity of growth) are also different for the two methods of growing metal crystals. Therefore the gas content need not necessarily be the cause or the only cause of the softness of the crystals made in air. But the results are interesting in so far as this seems a case where an *impurity* facilitates slip.

In connexion with the rotations which Dr Burgers has shown to take place in aluminium crystals if slip occurs, I wish to report a few results which were obtained on NaCl. The photograph (figure 4) shows four pictures of NaCl cleavage which were obtained by means of reflexion of X-rays from the cleavage. After one picture was taken the crystal was rotated  $30^\circ$  in the plane of reflexion. I shall not give the details of this method here\*. It is only necessary to state that these pictures are images of the cleavage in so far as one point on the photograph corresponds to one point only on the reflecting surface, and that the images would appear to be evenly illuminated if the crystal were perfect. The black and white stripes correspond to traces of the slip planes on the cleavage and show that some rotation has taken place near the plane of slip. The axis of rotation lies in the plane of slip and is perpendicular to the direction of slip. This corresponds to the results of Dr Burgers and to those obtained earlier by Prof. G. I. Taylor and C. F. Elam† on aluminium crystals. But there seems to be a difference in the interpretation of these results. Dr Burgers assumes cracks to be inside the crystals and explains the rotation by the action of these cracks. If it is permissible to generalize from the results on NaCl, we may say that this explanation can hardly hold, for the following reason: the rotation obtained on NaCl seems to be fairly uniform along the whole plane of slip. This is seen on the photograph, which is about natural size. One can also grind off a small amount from the surface and find the same rotation on a certain plane of slip if one goes into the crystal. To explain these rotations by cracks seems to be impossible. We might try to assume that there are very many small cracks of the same size, but even then it seems hard to imagine how they can produce a nearly uniform rotation all along the plane of slip. At least in the case of NaCl, another explanation must be found.

Again, I do not want to raise objections to G. I. Taylor's explanation of plasticity of crystals and of strain hardening, which seems to be a great step forward. I merely want to point out that there are facts connected with deformation by slip

\* See *Naturwiss.* 19, 391 (1931).

† *Proc. Roy. Soc. A*, 102, 643 (1923).

which still need further explanation. It may be that these facts are due to secondary effects.

There is the fact that we see slip bands at all. This fact means that two parts of the crystal have slipped one upon the other by a distance of several hundreds or thousands of atomic distances. We know that on NaCl crystals the occurrence of slip is marked by a stressed area along the plane of slip which shows itself by double refraction\*.

Further, a fairly uniform rotation takes place in the neighbourhood of the planes of slip in NaCl.

I used to explain these facts to myself by a complete breakdown of the crystal, whose two parts slip one upon the other by a distance of many atomic distances. Since the crystals obviously consist of many smaller "mosaic" crystals (purposely no further details will be given of what is meant by this expression, but that there is something like it is clear from the X-ray experiments of Darwin and others) these smaller parts experience different strains and stresses according to their relative position with respect to the actual plane of slip. They are rotated, leaving a strained and stressed area along the plane of slip. Of course, the main question is still open: Why does such a breakdown of the crystal occur?

For single crystals of tin it is known that slip occurs according to the change of shape of the crystal, but that sometimes no slip bands can be detected. This may be a case in which slip occurs purely according to Taylor's theory. Perhaps an extension of this theory, incorporating some assumptions about the mosaic nature of the common crystals, might account for some hitherto unexplained facts.

Sir R. HADFIELD. The paper by Prof. E. Schmid contains information of a particularly interesting kind to the metallurgist. The evidence he shows, that the shear strength of crystalline materials is not greatly increased by lowering of temperature, would however hardly seem to be consistent with that obtained from other sources as concerning steel and iron, from which it is believed that the shear strength is more greatly increased by low temperature than the cohesive or direct tensile strength. Consequently, the weakness to shear which occurs at ordinary temperature is not displayed at low temperature, i.e. temperatures of the order of that of liquid air ( $-182^{\circ}\text{C.}$ ), and breakdown occurs at these low temperatures by direct tension rather than by shear. This explanation it is believed also accounts for the brittleness and lack of ductility of iron and most steels at low temperature, since shearing is necessary to ductility.

Prof. Schmid's remarks on twinning are also of particular interest to the metallurgical microscopist. The readiness of twinned areas to re-crystallize would seem to imply that twinning must be regarded as an actual crystal breakdown just as much as an actual state of strain by movement along the slip planes. It is clearly an abnormal condition which the regular forces of crystallization dislike and do their best to rectify when an opportunity occurs as by raising the temperature.

It is not clear whether his figure 5 represents calculated or experimental results

\* I. W. Obreimoff and L. W. Schubnikoff, *Z. f. Phys.* **41**, 907 (1927).



for the various metals shown, or whether the data obtained by these two methods are in agreement. Certainly the fact that nickel shows in this diagram a pronounced hardening effect is in agreement with my own observations on this metal. If theory is in agreement with experiment then it would appear that very useful progress has been made in knowledge as to the cause of work-hardening which is found of so pronounced a degree in manganese steel.

Prof. A. SMEKAL. In connexion with the very interesting paper by Schmid, I should like to mention that Miss Dommerich in my institute has recently given measurements on the critical shear stresses for all three different slip systems of rock salt at ordinary temperature, and that the fact that these shear stresses are independent of crystallographic direction of deformation has been very well established in this case<sup>(1)</sup>. On the other hand, at much higher temperatures, Wolff was able to prove definitely the existence of gliding planes, which are in contradiction to the shear stress law<sup>(2)</sup>. Another interesting point which we have established on rock salt at ordinary temperature is a dependence of the operative slip systems on the form of cross-section of the monocrystalline rod. For instance, if we have to deal with tension perpendicular to a cube plane, four systems of dodecahedral gliding planes are equivalent. Nevertheless only those systems are realised for which the length measured along the gliding direction within the crystal is a minimum<sup>(3)</sup>. The origin for this new condition for slip is the fact that actual gliding starts from certain places within the crystal, and that the gliding planes tend to spread over the full cross-section with a definite velocity—facts which seem to be of great importance for all plasticity theories.

#### REFERENCES

- (1) S. DOMMERICH, *Z. f. Phys.* **90**, 189 (1934).
- (2) H. WOLFF, *Z. f. Phys.* **93**, 147 (1935).
- (3) A. SMEKAL, *Z. f. Phys.* **93**, 166 (1935).

Prof. E. SCHMID. I would like to add to the observations of Sir Robert Hadfield the following remarks which serve in the main to support his views.

(1) The fact that slip ceases in iron at low temperature does not compel the assumption that in this case the yield point rises particularly steeply with decreasing temperature. As Sir Robert remarks, the brittleness at  $-185^{\circ}\text{C}$ . is caused by the fact that before the elastic limit is reached another mechanism enters (cleavage parallel to the (100) plane, mechanical twinning parallel to (112)\*, with formation of cracks along this plane). The behaviour of iron thus demonstrates merely that the temperature change of these processes is less than that of the commencement of slip.

This receives a certain amount of confirmation from the scanty observational material at present available; the critical tension for tearing of bismuth and zinc crystals normal to the cleavage planes has been found to be independent of temperature.

(2) Examination of the atom distribution in the glide planes provides strong reasons for believing that the lattice is violently strained at the boundaries of twin

\* W. Fahrenhorst and E. Schmid, *Z. f. Phys.* **78**, 383 (1932).

lamellae\*. It is shown in this way, on purely geometrical grounds, that in many cases considerable distortion must occur.

(3) The hardening curves shown in figure 5 of my paper were determined experimentally. The first theoretical deduction of the curves was due to G. I. Taylor (reference (19) of my paper). According to his theory they should be parabolic, and in fact this is a good approximation to their form for the cubic metals.

As regards the remarks of Prof. Smekal, Miss Dommerich's work has interested me particularly, as in it the shear-stress law is applied to the determination of the slip-elements ((100) planes), in the same way as was attempted previously for iron crystals†. It appears to me however that no absolute proof has yet been given that slip on (111) planes also occurs in rock salt at room temperature, nor in particular of the critical shear stress on the third slip system, in the strict sense implied by Miss Dommerich.

As to the statement of Mr Wolff that slip occasionally occurs in rock salt which does not agree with the shear-stress law, any expression of opinion must be deferred until the work is published. I shall here only remark briefly that in the case of tin crystals also, for certain initial orientations, a slip system is found to be operative which would not be expected from the known values of the critical shear stress. The reason for this must be the very marked hardening which occurs on the missing slip system with increasing slip, as a result of which a system becomes operative‡ on which the hardening is much less. A decision as to whether such an explanation also accounts for Wolff's rock-salt results will only be possible when we are in possession of the hardening curves, as yet unknown.

\* See for example C. H. Mathewson, *Am. Inst. Min. Met. Eng.* (Feb. 1928).

† W. Fahrenhorst and E. Schmid, *Z. f. Phys.* **78**, 383 (1932).

‡ I. Obinata and E. Schmid, *Z. f. Phys.* **82**, 224 (1933).

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# International Conference on Physics

London 1934

INTERNATIONAL UNION OF PURE  
AND APPLIED PHYSICS

## REPORTS

ON

SYMBOLS, UNITS & NOMENCLATURE

APPROVED BY

THE GENERAL ASSEMBLY OF THE UNION

AT ITS

MEETING IN LONDON

ON

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# CONTENTS

<i>Preface</i>	v
I. The Standard Thermal Unit	3
II. Electrical and Magnetic Units	4
The International Electrotechnical Commission	6
Conclusions	7
<i>Appendix I. Electrical Units</i>	8
II. Alternative Methods on which to base Electromagnetic Quantities	11
III. Resolutions adopted by the I.E.C. at Oslo, 1930	16
IV. Convention as to Space Permeability	16
V. Modifications that might advantageously be introduced into certain magnetic formulae	17
VI. The m.k.s.Ω System	18
III. Certain Thermodynamic Symbols	20
IV. The Future Work of the S.U.N. Commission	23
V. Note sur ce que pourraient être les définitions des grandeurs magnétiques. By Prof. H. Abraham, Secretary of the Union	26
VI. The Force between two Elements of Current. By P. Vigoureux	38





## PREFACE

THE GENERAL ASSEMBLY of the International Union of Pure and Applied Physics was held in London on October 5, 1934, in connection with the International Conference on Physics, Professor R. A. Millikan being in the Chair. It was attended by Delegates from the National Committees adhering to the Union, and, by invitation, other members of the Conference. Representatives of the Electrical Terms and Definitions Committee of the British Association were also present by invitation.

A full account of the Proceedings will be issued in due course by the Secretary of the Union.

The present volume deals only with the Reports presented to the Assembly by Sir R. T. Glazebrook, President of the Commission on Symbols, Units and Nomenclature, and unanimously approved by the meeting, together with the supplementary notes arising out of these Reports.



# INTERNATIONAL UNION OF PURE AND APPLIED PHYSICS

## COMMISSION ON SYMBOLS, UNITS AND NOMENCLATURE

### INTRODUCTORY

At the General Assembly of the International Union of Physics at Brussels on July 12, 1931, a discussion took place on the definition of the Standard Thermal Unit. In the course of that discussion it became clear that definitions of many other standards in use in Physics were required, and a small Commission consisting of Prof. Kennelly, U.S.A.; Prof. Fabry, France; Prof. Keesom, Holland; and Sir Richard Glazebrook, Great Britain, was set up to deal generally with the subject of Symbols, Units and Nomenclature and to report to the International Union.

The Commission was given power to add to its numbers and to appoint its own Chairman.

Sir Richard Glazebrook was appointed Chairman and Dr Ezer Griffiths undertook the duties of Secretary. At a meeting in London shortly afterwards the Secretary of the Union was asked to write to the National bodies represented on the Union inviting them to nominate members to serve on the Commission. It was arranged also that the Commission, when discussing any special subject, would invite the assistance of experts cognizant of that subject, who would for that purpose become members of the Commission.

At the Meeting of the General Assembly on October 5, 1934, Prof. Millikan, President of the International Union of Pure and Applied Physics, was in the chair.

Four reports of the Commission on Symbols, Units and Nomenclature which had been approved by the Executive Committee of the Union at its meeting on October 1, 1934 were submitted by Sir Richard Glazebrook, President of the Commission, and, subject to minor changes of an editorial nature, were unanimously approved.

The reports concluded with the following recommendations\*:

#### I. THE STANDARD THERMAL UNIT

(a) That the Unit of Heat when measured in Units of Energy be the Joule defined as  $10^7$  ergs.

(b) That the Gramme-Calorie is the amount of heat required to raise the temperature of one gramme of water from  $14.5^\circ$  to  $15.5^\circ$  of the International Scale of Temperature under the pressure of one normal atmosphere.

\* The recommendations set out here are given in English. They will be printed in French in the official account of the Proceedings of the meeting, to be published by the Secretary of the Union.

## II. ELECTRICAL AND MAGNETIC UNITS

That Table 1 be accepted by the International Union of Pure and Applied Physics and that it be published as such.

Table 1. Electromagnetic units

Quantity designated	c.g.s. units			Practical units in terms of	
	Symbol	Defining equation	Name	c.g.s. units	Volt-ampere units
Flux	$\Phi$	$\frac{d\Phi}{dt} = -E$	Maxwell	$10^8$ Maxwells	Volt second
Magnetic Induction or Flux Density	$B$	$\int B dS = \Phi$	Gauss	$10^8$ Gauss	Volt second per $\text{cm}^2$
Magnetomotive Force round a circuit	$F$	$F = 4\pi NI$	Gilbert = Oersted cm.	$10^{-1}$ Gilbert	$1/4\pi$ ampere-turn
Intensity of Magnetizing Field	$H$	$\int H \cos \epsilon dl = F = 4\pi NI$	Oersted	$10^{-1}$ Oersted	$1/4\pi$ ampere-turn per cm. of path of $H$
Permeability	$\mu$	$\mu = \frac{B}{H}$	"Permeability"	$\frac{10^8 \text{ Gauss}}{10^{-1} \text{ Oersted}}$	$\frac{\text{Volt second per cm}^2}{1/4\pi \text{ ampere-turn per cm. length of path of } H}$

## III. CERTAIN THERMODYNAMIC SYMBOLS

(a) That Table 2 be put forward as a satisfactory series of symbols and nomenclature for the thermodynamic quantities referred to.

(b) That  $E$ ,  $\phi$  and  $I$  be accepted as alternative symbols for Internal Energy, Entropy and Heat Content respectively.

(c) That thermodynamic quantities should always be expressed in the Centigrade scale of temperature.

Table 2. Symbols for Thermodynamic Quantities

Name	Entropy	Internal energy	Free energy	Thermal potential or Gibbs function	Total heat, heat content or enthalpy	Work
Formula	—	—	$U - TS$	$U - TS + PV$	$U + PV$	—
Symbol	$S$ or $\phi$	$U$ or $E$	$F$	$G$	$H$ or $I$	$W$

In the above formulae  $P$  and  $V$  should be interpreted as representing a generalized force and generalized co-ordinate respectively.

## IV. THE FUTURE WORK OF THE S.U.N. COMMISSION

That the Commission on Symbols, Units and Nomenclature be authorized by the International Union of Pure and Applied Physics to continue its work on the lines indicated in the report.

For the notes and explanatory matter attached to these recommendations, reference should be made to the Reports which follow.

## I. THE STANDARD THERMAL UNIT

At the first meeting, July 12, 1931, the following recommendations to the General Assembly of the Union were approved: \*

(1) **That the Unit of Heat when measured in Units of Energy be the Joule defined as equivalent to  $10^7$  ergs.**

(2) **That the Gramme-Calorie is the amount of heat required to raise the temperature of one gramme of air-free water from  $14.5^\circ$  to  $15.5^\circ$  of the International Scale of Temperature under the pressure of one normal atmosphere.**

### *Note on Recommendation (2)*

According to existing measurements the gramme-calorie is equivalent to  
 $4.18_6$  Joules.

This definition is consistent with the decision of the International Steam Tables Conference in 1929 to adopt as a Unit suitable for their purpose an International Kilo-Calorie equivalent to  $1/860$  of an International Kilo-Watt Hour.

The relation\* between the International Watt-second and the Joule is given by

$$1 \text{ International Watt-second} = 1.0003 \text{ Joules.}$$

The Commission on Symbols, Units and Nomenclature recommend:

**That this statement be adopted by the General Assembly of the Union, and that they be authorized to publish it.**

The Commission are indebted to Dr Wallot, Secretary of the Ausschuss für Einheiten und Formelgrossen, for the information that the conclusions under (1) and (2) agree with the German law of 1924 relating to the Unit of Heat. In the German law only the International Unit is referred to, and the words "at atmospheric pressure" are added.

\* This figure differs from that [1.00039] given earlier. Recent determinations of the ratios International Ampere/Ampere and International Ohm/Ohm have been made at the American Bureau of Standards, Washington, and at the National Physical Laboratory, Teddington, which lead to the following results for the ratio International Watt-second/Joule;

$$\begin{aligned} \text{B.S. } &1.00031, \\ \text{N.P.L. } &1.00025. \end{aligned}$$

The International Steam Tables Conference Meeting in New York in September 1934 chose for its own purposes 1.0003 as the ratio of the International to the absolute Joule.

The S.U.N. Commission therefore recommends that for the present the figure 1.0003 be accepted. The whole question of the ratio of the International to the c.g.s. units of electrical quantities is now under the consideration of the Electrical Committee of the International Convention of Weights and Measures. Any final figure for the value of the International Watt-second must await the decision of the Convention.

## II. ELECTRICAL AND MAGNETIC UNITS

AT the meeting of the S.U.N. Committee in London on September 22, 1931, co-operation with the Standards Committee of the International Electro-Technical Commission—Chairman, Prof. Kennelly—and with the Committee of the British Association on Electrical Units—Chairman, Sir James Henderson—was arranged for and it was agreed generally to make Electrical and Magnetic Units the first subject of investigation by the Commission. Accordingly a questionnaire\* was drawn up and sent to the National Committees of the Union and to other parties interested.

The principal issues raised by the questionnaire related to (1) the basis on which to rest a connected account of electro-magnetic phenomena, (2) should  $\mu$ , the permeability, be treated as a quantity having dimensions in mass, length and time or as a pure number?

The various National bodies were asked to reply by a certain date and much interesting information was obtained.

An Electrical Congress was held in Paris during July 1932, and it was thought desirable to take the opportunity of the presence of electricians from many nations to hold an informal conference between representatives of the International Union of Physics and of the National Committees of a number of countries. This took place on July 9th; the conference was attended by representatives from Belgium, France, Great Britain, Germany, Holland, Italy, Norway and the United States†.

The following propositions were unanimously accepted by the conference:

(1) Any system of units recommended must retain the eight internationally recognized practical units, viz. joule, watt, coulomb, ampere, ohm, volt, farad, henry‡.

(2) The c.g.s. system of units is suitable for the physicist.

(3) The system of practical units, including the above eight quantities, is derived from this by multiplying the c.g.s. unit by appropriate powers of 10.

A majority of those present expressed themselves in favour of the following propositions:

(4)  $B$  and  $H$  are quantities of different kinds.

(5) The factor  $4\pi/10$  should be retained in the practical definition of magnetomotive force.

\* See Appendix I.

† Sir Richard Glazebrook, Chairman (Great Britain).

Prof. Wilberforce (Great Britain).

Dr Ezer Griffiths, Secretary (Great Britain).

Prof. Abraham (Secretary of Union of Physics) (France).

Prof. Fabry (France).

Prof. Paul Janet (France).

Prof. Brylinski (France).

Prof. Cotton (France).

Prof. Liénard (France).

Prof. Bunet (France).

Prof. Verschaffelt (Belgium).

Prof. van Staveren (Holland).

Prof. van der Well (Holland).

Prof. Wallot (Germany).

Prof. Lombardi (Italy).

Prof. Bjerknes (Norway).

Prof. Kennelly (U.S.A.).

Prof. Pender (U.S.A.).

Dr Curtis (U.S.A.).

‡ The following definitions of electrical units are implied:

1 volt =  $10^8$  c.g.s. units.

1 ampere =  $10^{-1}$  c.g.s. units.

1 ohm =  $10^9$  c.g.s. units.

(6) The system of magnetic units may be based on the following two methods as alternatives†:

- (a) The force between two elementary magnetic poles (Coulomb).
- (b) The force between two elements of current (Ampère).

Some members of the Conference were in favour of:

- (c) A system based on the magnetic flux.

The conference was quite informal, and was intended to guide the S.U.N. Commission in the preparation of its report to the International Union of Physics, which it was hoped would meet in Chicago in 1933.

Table 1‡ gives effect to the conclusions stated in (1) to (6).

Table 1. Electromagnetic units

Quantity designated	c.g.s. units			Practical units in terms of	
	Symbol	Defining equation	Name	c.g.s. units	Volt-ampere units
Flux	$\Phi$	$\frac{d\Phi}{dt} = -E$	Maxwell	$10^8$ Maxwells	Volt second
Magnetic Induction or Flux Density	$B$	$\int B dS = \Phi$	Gauss	$10^8$ Gauss	Volt second per $\text{cm}^2$
Magnetomotive Force round a circuit	$F$	$F = 4\pi NI$	Gilbert = Oersted cm.	$10^{-1}$ Gilbert	$1/4\pi$ ampere-turn
Intensity of Magnetizing Field	$H$	$\int H \cos \epsilon dl = F = 4\pi NI$	Oersted	$10^{-1}$ Oersted	$1/4\pi$ ampere-turn per cm. of path of $H$
Permeability	$\mu$	$\mu = \frac{B}{H}$	"Permeability*"†	$\frac{10^8 \text{ Gauss}}{10^{-1} \text{ Oersted}}$	$\frac{\text{Volt second per cm}^2}{1/4\pi \text{ ampere-turn per cm. length of path of } H}$

\* The unit of "permeability" on the c.g.s. electromagnetic system is the permeability of free space—in practice that of the air. This unit has received no special name. The statement that the permeability of a given medium is  $\mu$  implies that it is  $\mu$  times  $\mu_0$ , the permeability of free space, which on this system has the value unity.

Complete agreement as to the definitions of  $B$  and  $H$  has not yet been reached. For the definition of  $B$  we are not far from it, but the definition of  $H$  still remains somewhat uncertain. If in the future, definitions should be adopted which would imply that  $B$  and  $H$  are quantities of the same kind, Table 1 would still hold.

It would then be understood that the names Gauss and Oersted were two different names given to the same quantity determined by experiment. In these circumstances either the one or the other of the two synonymous words might be employed as found more convenient.

The Commission are indebted to Dr Wallot, Secretary of the Ausschuss für Einheiten und Formelgrossen, for the information that the conclusions of Table 1, except for the insertion of  $4\pi$ , agree completely with those of the German Association for Units.

In the questionnaire originally issued the hope was expressed that it might be possible to find an agreed basis for the definition of electromagnetic quantities.

† Further details as to these will be found in Appendix II.

‡ In the Table,  $dS$  is an element of area through which the induction is  $B$ ;  $dl$  an element of length along which  $H$  is integrated, and  $\epsilon$  the angle between  $H$  and  $dl$ .



Prof. Abraham was asked to prepare a memorandum on the subject\*.

During the past three years the various suggestions for such a basis have been discussed, but it is not yet the case that a scheme securing general assent has emerged. Although, however, the formulation of such a scheme would be highly desirable, progress is possible in its absence, and without prejudicing any future decision between the alternatives (a), (b) or (c) or any combination or modification of them, we can state that Table 1 may be accepted as defining the units in terms of which the electromagnetic quantities required for practical purposes are measured.

The question of "rationalization" is briefly considered later in the report. Should it be adopted, certain changes will be required in the Table.

## THE INTERNATIONAL ELECTROTECHNICAL COMMISSION

In October 1933 a meeting of the International Electrotechnical Commission was held in Paris under the chairmanship of Dr Kennelly, at which certain important decisions indicated below were arrived at. These are given below for the information of the International Union of Physics.

### (i) *Definition of Magnetic Units*

At the meeting of the Commission in Oslo in July 1930 a series of definitions of magnetic units had been adopted. These were confirmed at Paris† with the addition to the definition of  $B$ , the magnetic flux density, of the words "The value of the flux density at a point may be evaluated either by the mechanical force exerted on an element of a conductor carrying a current placed at the point or by the electromotive force produced in an elementary circuit surrounding the point."

### (ii) *Permeability of Space*

Attention should also be drawn to a recommendation unanimously agreed to in principle that in view of the convention‡ concerning the nature of space permeability adopted at Oslo in 1930, the symbol  $\mu_0$  be inserted in various working magnetic formulae§.

### (iii) *Professor Giorgi's Proposals*

A full discussion also took place on the proposals of Prof. Giorgi as to the m.k.s. system of units||, and it was agreed to invite the National Committees of the I.E.C. "to give their opinions on the extension of the series of practical units by its incorporation in a coherent system having as fundamental units of length, mass and time the metre, kilogramme and second and as a fourth fundamental unit either that of resistance expressed as the precise multiple— $10^9$ —of the c.g.s. electro-magnetic unit or the corresponding value of the space permeability of a vacuum."

\* The first part of this has been printed with the title "A propos des Unités Magnétiques" in the *Bulletin de la Société Française des Électriciens*, the second part will be found on p. 26.

† The definitions as modified at Paris are given in Appendix III, p. 16.

‡ For a statement of this see Appendix IV, p. 16.

§ For these formulae see Appendix V, p. 17.

|| For an account of this see Appendix VI, p. 18.

It should be noted that both these alternatives differ from Prof. Giorgi's original proposal, which was to adopt as the fourth fundamental unit the resistance of a material standard such as a tube of mercury or a wire of some metal.

Omitting for the present the question of rationalization which is also part of Prof. Giorgi's original proposal, neither is inconsistent with the c.g.s. system which suffices for physicists.

According to the c.g.s. electromagnetic system, the permeability of a vacuum is unity. If electrotechnical engineers prefer a system in which the value is taken as  $10^{-7}$  or in which  $10^9$  c.g.s. units of resistance are treated as an absolute unit, neither alternative will make any difference in our practical standards.

#### (iv) *Rationalization*

A decision as to "Rationalization" and the omission of the  $4\pi$  in the definition of magnetomotive force was left open for the present "in view of the different views held by different countries."

### CONCLUSIONS

The above recommendation as to rationalization raises the question what should be the action of the S.U.N. Commission in the matter.

At the Paris Conference in 1932 it was pointed out that  $\pi$ , the ratio of the surface of a sphere to the square of its diameter, must occur somewhere in the formulae. Thus on a rationalized system the force between two charges  $e, e'$ , would be given as  $ee'/4\pi kr^2$ . Observation tells us that the force varies as  $1/r^2$  but does not indicate any reason for the presence of the  $4\pi$ .

As it appears improbable that an overwhelming preponderance of opinion either favourable or unfavourable to rationalization will be manifested in the near future, it is undesirable that the Union should defer action with regard to Electromagnetic Units until agreement on this particular matter has been reached. The present electromagnetic system is based on the selection of unity as the value of  $\mu_0$ ; and, while realizing that there would have been a simplification in certain engineering formulae had the magnitude originally selected been  $1/4\pi$ , the Commission on Symbols, Units and Nomenclature recommends that the present convention be continued until there is a definite preponderance of opinion in favour of a change.

Accordingly the Commission is of opinion that, in the present condition of knowledge, the series of propositions in Table 1 on p. 5 of this Report forms a satisfactory basis for physicists for the definition of Electromagnetic Units.

The Commission recommends, therefore,

**That Table 1 be accepted by the International Union of Pure and Applied Physics as defining Electromagnetic Units and that it be published as such.**

The Commission have learned with much disappointment that Dr Kennelly, to whose devoted work in connection with Standards and Units, electrical science is so deeply indebted, is prevented from attending the London meeting of the

Union. He is at present recovering from the effects of a serious operation to his eyes.

They trust that he may in a short time be restored to his usual health and have requested the President to cable to him a message expressing their sympathy and regrets.

#### APPENDIX I. CIRCULAR OF 1931

### COMMISSION FOR SYMBOLS, UNITS AND NOMENCLATURE

#### ELECTRICAL UNITS

The systems of units now universally employed in Electric and Magnetic Measurements are based on the c.g.s. system and had their origin in the Reports of the Committee on Electrical Standards of the British Association. Their early history is contained in Appendix C to the second Report of that Committee in 1863, which was drawn up by Maxwell and Fleeming Jenkin.

These systems were further developed by Maxwell in his *Treatise on Electricity and Magnetism* published in 1873. They are known as the Electrostatic and Electromagnetic systems of units. The electrostatic system is based on the deductions drawn from Coulomb's experiments concerning the law of force between two small bodies charged with electricity. The electromagnetic system is based on the law of force between two magnetic poles which was deduced from similar experiments with magnets, on Oersted's discovery of the force between an electric current and a magnetic pole, Ampère's experiments on the force between two current-carrying circuits and Faraday's discovery of electromagnetic induction. Magnetization by induction is referred to in Appendix C (Section 9) but its consequences are not further developed.

On the assumptions actually made in the appendix the dimensions of the various electric and magnetic quantities are worked out on these two systems, and it is shown that the ratio of the units involved depends on a velocity which experiment has proved to be that of light.

In the *Treatise* Maxwell extends the results to include magnetic media and, following Sir William Thomson\*, introduces "Magnetic Induction" defined as the force on unit positive pole placed in a crevasse in the medium cut at right angles to

\* [Note added Nov. 1934, by Sir R. T. Glazebrook.] In his twenty-sixth series of Researches (Nov. 1850) Faraday refers to experiments which he says "have led me to the idea that if bodies possess different degrees of *conducting power for magnetism* that difference may account for all the phenomena." Twenty-two years later Sir W. Thomson, in a paper on "Magnetic Permeability and Analogues in Electrostatic Induction, Conduction of Heat and Fluid Motion" (*Papers on Electrostatics and Magnetism*, p. 482), after a reference to Faraday's paper, introduces the term "magnetic permeability, a synonym for conducting power for lines of magnetic force," and obtains the relation  $\mu = 1 + 4\pi\kappa$  between the permeability  $\mu$  and the susceptibility  $\kappa$  of a substance.

Maxwell, in §428 of his *Treatise* when dealing with the theory of induced magnetism from what he considers "to be Faraday's point of view", writes "When magnetic force acts on any medium. . . it produces within it a phenomenon called Magnetic Induction."

"Magnetic induction is a directed quantity of the nature of a flux. . ."

"In isotropic media the magnetic force and the magnetic induction are in the same direction, and

the lines of force. Magnetic Force is defined as the force on a unit positive pole in an infinitely narrow long cylinder parallel to the lines of force—Sir William Thomson's Polar definition of Magnetic Force. Magnetic induction has therefore on this view the same dimensions as magnetic force and their ratio denoted by the symbol  $\mu$  is a pure number. In developing the equations of the magnetic field the quantity  $\mu$  is retained (Sections 614, 615) with the statement that on the electromagnetic system of units it is only within magnetized matter that it has a value different from unity and that, on that system therefore, its value in a vacuum is unity. On that system it has no dimensions.

This identification of magnetic induction and magnetic force appears to be the cause of some of the difficulties and misunderstandings which have arisen in regard to the subject and have led in many countries to suggestions for some modification of the fundamental conceptions.

Another difficulty arises from the fact that in accordance with Maxwell's definitions  $4\pi$  occurs in the measure of certain electrical quantities; attempts have been made to modify the definitions and to produce a "Rational system" of units which does not expressly involve  $4\pi$ .

Probably, however, a difficulty which is more seriously felt arises from the fact that there is no such thing as a single isolated magnetic pole. Neither can we realize a single particle charged with a quantity  $e$  of electricity\*.

The Commission on Symbols, Units and Nomenclature of the International Union of Physics has been set up in order to facilitate discussion and if possible secure agreement on matters relating to units of International importance. The discussions which have for some time been in progress in many countries on Electrical Units and Nomenclature and the existence of a Committee of the International Electrotechnical Commission, dealing specially with the side of the question of interest to Engineers, are sufficient evidence of the importance of the subject and of the need for its discussion by physicists.

the magnetic induction is the product of the magnetic force into a quantity called the coefficient of induction, which we have expressed by  $\mu$ ."

"In empty space the coefficient of induction is unity. In bodies capable of induced magnetization the coefficient of induction is  $1 + 4\pi\kappa = \mu$ , where  $\kappa$  is the quantity already defined as the coefficient of induced magnetization."

Earlier in the work (§400), Maxwell had defined Magnetic Induction as "the force within a hollow disc, whose plane sides are normal to the direction of magnetization."

It should be noted that Thomson nowhere applies the name Induction to the quantity thus defined by Maxwell, i.e. the vector  $\mathfrak{B} = \mathfrak{H} + 4\pi\mathfrak{I}$ ; to him this is the electromagnetic definition of magnetic force.

Maxwell repeats this definition of Induction in §604. It is the "force which would be exerted on a unit pole, if placed in a narrow crevasse in the body, the walls of which are perpendicular to the direction of magnetization."

In §614, however, " $\mu$ , the coefficient of magnetic permeability" is introduced, and we have  $\mathfrak{B} = \mu\mathfrak{H}$ , as in the statement already quoted from §428.

This is the definition now generally accepted, the symbol  $\mu_0$  being employed to denote the permeability of free space.

The apparent inconsistency between some of these statements disappears if we recollect that on the electromagnetic system of units, the value of  $\mu_0$  is unity.

It may be noted that in §618 the magnetic permeability  $\mu$  is called by Maxwell "the magnetic inductive capacity" of a medium.

\* This was written in 1931.

Accordingly at a recent meeting of the S.U.N. Commission it was agreed to ask the National Committees of Physicists adhering to the Union to obtain from representative bodies and persons in their respective countries their views on the matter with suggestions as to a series of definitions and units which might replace those based on Maxwell's system as to which difficulty is felt, and to send these to the Symbols, Units and Nomenclature Commission.

In replying to the enquiry it should be realized that it is essential that any new definition or scheme should, with the definitions retained from Maxwell, if any, form a consistent whole, covering all the physical quantities in ordinary use. Starting as Maxwell does from the force between two poles or possibly from Ampère's results as to the force between two circuits carrying currents or from some other fundamental properties the series of definitions should build up a consistent logical system, in which the various quantities employed are capable of measurement to the accuracy called for by modern electrical science.

It may be of assistance to indicate some of the suggestions which have been made to meet the difficulties: (1) Dealing with a complete system, we may write for the electrical force between two charged particles  $ee'/\kappa r^2$ , and for the magnetic force between two poles  $mm'/\mu r^2$ , where  $\kappa$  and  $\mu$  have dimensions and are such that  $1/\mu\kappa$  is the square of the velocity of light in the medium considered. A consistent system can be derived from this, following Maxwell's lines, but without further knowledge the dimensions of a quantity of electricity or of a magnetic pole are both indeterminate. Moreover, the system is based on the assumed result of experiments which cannot be completely realized; an isolated magnetic pole does not exist.

According to Maxwell, on the electrostatic system  $\kappa$  has no dimensions while those of  $\mu$  are  $T^2/L^2$ ; on the electromagnetic system  $\mu$  has no dimensions but those of  $\kappa$  are  $T^2/L^2$ .

Various modifications in Maxwell's scheme have been suggested to meet some of the above difficulties and to avoid the introduction of the  $4\pi$  which appears in some of the equations.

(2) Dealing with magnetic units only we may start from definitions of magnetic flux given by the expression  $\int_0^t E dt$ , where  $E$  is the electromotive force in volts round a circuit through which the flux is measured and magnetomotive force  $= NI$ , where  $I$  is current in amperes and  $N$  a numeric. Such a method assumes that we have defined and can measure volts and amperes.

As another example the following statement as to magnetic induction may be given—Magnetic flux per unit area is measured by removing from a magnetic field a small circular coil of wire having a single turn of area  $S$  and resistance  $R$  and measuring the quantity  $Q$  of electricity which flows round the circuit. The magnetic induction normal to the circuit is given by  $B = RQ/S$ .

This is in effect the same as the method given above and implies that we have defined and can measure  $Q$  and  $R$ .

APPENDIX II

*Alternative methods on which to base Electromagnetic Quantities*

(a) THE FORCE BETWEEN TWO MAGNETIC POLES\*. (COULOMB; MAXWELL.)

$$\text{Force} = \frac{ee'}{\kappa_0 r^2} \quad \dots\dots(1).$$

$$\text{Force} = \frac{mm'}{\mu_0 r^2} \quad \dots\dots(2).$$

$$\text{Force} = \frac{mi \sin \theta ds}{Ar^2} \quad \dots\dots(3).$$

The forces being measured in free space, practically in air, whence  $A^2/\mu_0\kappa_0 = (\text{velocity})^2$ . The velocity can be shown to be that of electromagnetic waves.

Also  $A$  is constant for all media. Maxwell puts  $A=1$  and alternatively  $\kappa_0=1$  (electrostatic system) or  $\mu_0=1$  (electromagnetic system).

In Gauss' system  $A=c$ , the velocity of wave propagation in free space, while  $\mu_0$  and  $\kappa_0$  are pure numbers having no dimensions. In a more general case  $\mu_0$  and  $\kappa_0$  are constants of unknown dimensions, but such that

$$\frac{A^2}{\mu_0 \kappa_0} = c^2.$$

Again it follows from the equation (3) that the potential energy of a pole  $m$  in the neighbourhood of a circuit carrying a current  $i$  is  $mi\omega$ , where  $\omega$  is the solid angle subtended by the circuit at the pole. The magnetic flux  $\phi$  through any circuit is connected with the e.m.f.  $E$  set up in the circuit by changes in the value of  $\phi$  by the equation  $\phi = -\int E dt$ .

Consider now a circuit in the form of a circle and let a magnetic pole  $m$  approach the circuit along the axis of the circle. In time  $dt$  the work done against the field will be  $mi \frac{d\omega}{dt} dt$ .

If we may assume that energy is not drawn from any non-electrical source, then to keep the current constant, work must have been done requiring an additional e.m.f. in the circuit and, since in time  $dt$  the quantity of electricity which has passed is  $i dt$ , the electromotive force necessary is the work done against the field, divided by  $i dt$ , i.e. it is  $-\frac{m d\omega}{dt}$ .

Thus the flux through the circle due to the pole is

$$\int m \frac{d\omega}{dt} dt \text{ or } m\omega,$$

and the induction through a spherical surface with the pole as centre, passing through the circle, will be  $m\omega/r^2\omega$  or  $m/r^2$ .

\* Or alternatively two point charges.

Thus in the case of a single pole  $m$  we have

$$H = \text{magnetic force} = \frac{m}{\mu_0 r^2},$$

$$B = \text{magnetic induction} = \frac{m}{r^2},$$

$$\text{or } B = \mu_0 H.$$

This result holds for each of the poles of which we suppose any distribution of magnetism to consist, hence we have generally that in free space  $B_0 = \mu_0 H$  and in a medium in which the permeability is  $\mu_1$ ,  $B_1 = \mu_1 H$ .

Thus  $B_1/B_0 = \mu_1/\mu_0 = \mu$  the specific permeability, and in general  $B_1 = \mu B_0$ , where  $\mu$  is a number having no dimensions.

In a medium magnetized so that the magnetic moment of an element  $dv$  is  $I dv$  we still have  $B_1 = \mu_1 H$ , where  $\mu_1 = \mu_0 \left( 1 + \frac{4\pi I}{\mu_0 H} \right)$ . Thus writing  $I = \kappa H$  we have

$$\mu_1 = \mu_0 \left( 1 + \frac{4\pi \kappa}{\mu_0} \right)$$

so that the specific permeability is given by

$$\mu = \frac{\mu_1}{\mu_0} = 1 + \frac{4\pi \kappa}{\mu_0}.$$

In a non-magnetic medium or one that is only slightly magnetic  $\kappa$  is zero or a constant; in magnetic media it depends on the value of  $H$  and in this case  $\mu$  is a function of  $H$ .

(b) THE FORCE BETWEEN TWO ELEMENTS OF CURRENT. (AMPÈRE.)

$$\text{Force} = i' \sin \psi' ds' \cdot |ri \sin \theta ds|$$

This represents the force on an element  $i' ds'$  arising from the action of a current  $i$  in a closed circuit of which an element is  $ds$ ,  $\theta$  representing the angle between  $ds$  and  $r$ ,  $\psi'$  that between  $ds'$  and the magnetic force, and the vertical lines denoting vectorial integration\*.

From the point of view developed here, it is possible to describe all magnetic phenomena as due to the action of atomic currents, without the introduction of any other notion than that of magnetic induction.

At any given point of a magnetic body a distinction is drawn between the induction due to distant currents, which varies gradually from point to point, and the induction produced by local currents to which are due the rapid changes of the total induction in the neighbourhood of these local currents; we are thus led to consider the mean total induction at a point (a vector  $B_2$ ) which is the sum of the mean

\* The seven paragraphs which follow constitute an outline of the arguments developed in the "Note sur ce que pourraient être les définitions des Grandeurs Magnétiques" prepared by Prof. H. Abraham for the Commission at the request of the Conference of July 1932, and published as a supplement to this report. Prof. Abraham desires to state that the note is based in great measure on the work of Prof. Liénard.

induction due to all the local currents (a vector  $B_1$ ) and the induction due to the distant currents—the magnetizing induction—(a vector  $B_0$ ). Thus  $B_2 = B_0 + B_1$ .

The vector  $B_2$  is conservative. The vector  $B_0$  is derived from a potential of which the singular lines are the electric currents with  $\oint B_0 dl = \alpha I$ , where  $I$  is the current and  $\alpha$  a numerical coefficient depending on the units. As to the vector  $B_1$  it is proportional to the mean of the vector  $(SI)$ ,  $S$  being the area of the circuit in which the local current  $I$  circulates.

Defining intensity of magnetization  $\mathcal{A}$  by the relation

$$\mathcal{A} = \gamma (SI)_{\text{mean}},$$

where  $\gamma$  is a numerical coefficient, we have for the induction due to local currents,  $B_1 = \alpha \mathcal{A} / \gamma$ , where  $\alpha$  is another numerical coefficient. The equation  $B_2 = B_0 + B_1$  then becomes  $B_2 = B_0 + \alpha \mathcal{A} / \gamma$ .

In addition we have the coefficient  $\beta$  required to express the relation between the magnetic induction and the induced current given by the equation

$$E = \beta \frac{d\phi}{dt},$$

where  $\phi = \oint B dS$ , and the constant  $\mu_0$  introduced by the formula of the older theory  $F' = mm' / \mu_0 r^2$ , which expresses Coulomb's law. These four constants  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\mu_0$  are connected by a relation which follows when the expressions for the force between two magnets in the classical and the new notation are equated. It is found that  $\alpha\beta\mu_0 = 4\pi\gamma^2$ .

Moreover a magnet of magnetic moment  $\mathcal{M}$ , which is equal to  $\gamma \Sigma SI$ , when placed in a uniform field of induction  $B$ , is subject to a couple

$$C = \frac{\beta}{\gamma} B \mathcal{M}.$$

Finally the vector  $B_2$  is identified with the magnetic induction  $B$  and the vector  $B_0$  (for which the name *magnetizing induction* is suggested) is identified with the vector usually denoted by  $H$ .

If we define by  $R ds$  the force on an element  $ds$  and integrate along a circuit of which an element is  $dl$  inclined at an angle  $e$  to the direction of  $R$  we can show that

$$\int_{\perp}^B R \cos e dl = \mu_0 i (\Omega_B - \Omega_A),$$

where  $\Omega$  is the solid angle subtended at  $ds'$  by the closed circuit of which  $ds$  is an element.

If we integrate round a complete circuit which encloses  $i$  we obtain

$$\oint R \cos e dl = 4\pi\mu_0 i.$$

Identifying  $R$  with  $B$ , the magnetic induction, and writing  $B = \mu_0 H$ , we have  $\oint H \cos e dl = 4\pi i$ .

### (c) A SYSTEM BASED ON MAGNETIC FLUX.

1. The object of this system is to provide a method of deriving a system of units that shall be free from theoretical abstractions like the unit pole, and that shall be



capable of verification by the ordinary student in an ordinary laboratory. It depends almost entirely upon the work of Faraday.

2. Unit quantity (the coulomb) is defined first, and, as in law, is based upon electrolytic phenomena. The ampere follows as a flow of one coulomb per second. Then there are three alternatives. Some writers base the unit of potential difference upon the work of Joule and Kelvin, in which case the volt becomes the potential difference existing between two points of a circuit where one joule of work is done in the transfer of one coulomb; and the unit of resistance follows from Ohm's law. Others adopt the standard legal column of mercury as the arbitrary unit of resistance, from which the volt is deduced by Ohm's law. Finally, the requisite fraction of the potential difference of a cadmium cell is occasionally used to define the volt arbitrarily.

3. The unit of capacity follows from the volt and coulomb, and this, together with the experiments of Cavendish and Faraday, enables measurements to be made logically with electrostatic instruments. Hot wire instruments are of course available, since they depend on quantities already defined. (Electric field intensity is measured in volts per cm. and the absolute dielectric constant for a vacuum is  $8.84 \times 10^{-14}$  coulomb per volt cm. measured experimentally.)

4. The magnetic units are based upon the laws of electromagnetic induction, which show that associated with every electric circuit there is a field of electromagnetic momentum extending far beyond the actual conductor. This momentum is measured in volt seconds, and its time-rate of change is electromotive force (e.m.f.) in volts. At any part of the field (in a vacuum or in air) the maximum momentum established in a secondary coil of unit area and one turn by the interruption of the primary current is taken as the induction density  $B$  at that part. The instrument for measuring momentum is a long period electrometer. The value of  $B$  integrated over a normal section of the field is the total flux of momentum  $\phi$ . This is measured in volt seconds by a single-turn secondary embracing closely the primary and attached to the electrometer. In air or a vacuum,  $\phi$  is found to be proportional to the primary current, so that  $\phi = LI$ , where  $L$  is constant.  $B$  can be plotted as a vector at each part of the field, when the resulting vector chains represent a series of tubes of momentum, which are found to be continuous and linked with the primary like the magnetic curves depicted by iron filings.

Similar measurements made in magnetic fields in which  $B$  is uniform (long solenoid, thin toroid, etc.), show that in air  $B$  and the ampere-turns per unit length of the primary,  $H$ , are proportional. The factor of proportionality is  $\mu$ , the permeability of the medium, which in air (or a vacuum) has the experimental value  $1.256 \times 10^{-8}$  volt second per ampere cm. Again,  $B \times H = \text{joules per unit volume}$ .

Further  $\int H dl$  along any path in the field is termed the magnetomotive force (m.m.f.). It can be measured by means of a secondary spiral of uniform area  $A$  and  $n$  uniform turns per cm. attached to the ballistic electrometer. When the primary current is interrupted, this device measures the momentum appropriate to the path of the spiral; and since for each element of the spiral  $B = \mu H$ , it follows that  $\int H dl$

is obtained from the measured volt seconds divided by  $\mu An$ . The three cardinal expressions for the line integral are thus experimentally derived, viz.:

- (a) The m.m.f. between any two points is independent of the path.
- (b) The m.m.f. of a closed path is zero unless it embraces a current.
- (c) The m.m.f. of any closed path embracing ampere-turns  $NI$  is itself  $NI$ .

5. Turning to magnetic circuits containing iron, it is easy to show that an iron core in a solenoid has the same effect as an increase of ampere-turns of the solenoid. The presence of the solenoid rotates the elementary invisible molecular currents in the iron so that they are added to the visible primary ampere-turns. Thus in a complete iron circuit  $B$  is now  $1.256/10^8$  times the sum of  $H$  due to the coil and  $H$  due to the iron. This is commonly expressed by saying that  $B = \mu_1 \times (H \text{ due to the coil})$  and giving  $\mu_1$  a new value. While this convention gives no rational explanation of paramagnetism, it has been so widely adopted as to make a change difficult. But actually a more rational device would be to replace the ordinary  $B$ - $H$  curves for iron by curves between  $H$  for the coil and  $H$  for the coil plus the iron. The latter multiplied by  $1.256 \times 10^{-8}$  would then give  $B$ , and  $\mu$  becomes a universal constant connecting ampere-turns with momentum expressed in volt seconds per ampere cm.

6. An alternative to the measurements in (4) above is to close the unit secondary coil through a ballistic ammeter and measure the maximum integrated current when the primary circuit is broken. This quantity multiplied by the resistance of the secondary circuit again gives the electromotive momentum as in the first method.

7. The electromagnetic momentum generated in a secondary coil near a primary carrying a current  $I$  may be written  $MI$  when the primary current is interrupted; and since e.m.f. = the rate of decrease of momentum we get  $E = -d(MI)/dt$ . To generate an e.m.f. then in the secondary, either  $M$  or  $I$  or both may be changed. Now  $L$  and  $M$  depend only on the form and relative position of the circuits. Thus an e.m.f. may be induced either by mechanical movement  $-(I\dot{M})$ , or current change  $-(M\dot{I})$ , or both. The first covers most generators, the second all transformers and the third certain a.c. motors.

Summarizing the above, it will be seen that in this system:

(i) Electrical quantity is regarded as fundamental and its unit is based on electrolytic effects (the coulomb).

(ii) Current is quantity per second (the ampere).

(iii) The e.m.f. unit is derived from the heating effect of a current (the volt).

(iv) Resistance is the ratio of (iii) to (ii); alternatively, the unit of resistance (the ohm) may be arbitrarily adopted and the unit e.m.f. derived from that and the unit of current.

(v) The unit of magnetomotive force is unit current passing through a single turn (the ampere-turn).

(vi) The unit of flux density is that flux which when removed from a turn embracing one sq. cm. sets up unit electromagnetic momentum (the volt second).

(vii) The unit of field intensity is one current-turn per cm.

(viii) Permeability is an experimentally derived quantity. It is the ratio of the flux density to the field intensity. It is expressed in volt seconds per ampere cm.

The whole of the above can be experimentally demonstrated in the laboratory and no appeal is made to permanent magnets or magnetic poles. The former are regarded as special solenoids, and the latter as places where in a magnetic circuit the character of the medium changes.

### APPENDIX III

#### *Resolutions adopted by the I.E.C. at Oslo, 1930*

The magnitude  $H$  (Magnetic Field-Strength or briefly Magnetic Field) is the quotient of the mechanical force exerted by the magnetic field on a quantity of magnetism divided by that quantity.

The magnetic flux density  $B$  is a vector which represents in magnitude and direction the state of total polarization due to a magnetic field.

(Addition made at Paris, 1933). The value of the flux density at a point may be evaluated either by the mechanical force exerted on an element of a conductor carrying a current placed at the point or by the electromotive force in an elementary circuit surrounding the point.

The permeability  $\mu$  is equal to the ratio of the magnetic flux density  $B$  to the magnetic field strength at the point

$$\mu = \frac{B}{H}.$$

The magnetomotive force  $F$  is the integral of the magnetic field strength  $H$  along a line

$$F = \int H dl.$$

The magnetic flux  $\phi$  passing through an area  $S$  is the integral of the induction  $B$

$$\phi = \int B dS.$$

### APPENDIX IV

#### *Convention as to Space Permeability—resolutions adopted by the I.E.C. at Oslo, 1930*

That the formula  $B = \mu_0 H$  represents the modern concepts of the physical relations for magnetic conditions *in vacuo*, it being understood that in this expression  $\mu_0$  possesses physical dimensions.

In the case of magnetic substances the above formula becomes  $B = \mu_1 H$  in which  $\mu_1$  has the same dimensions as  $\mu_0$ . It follows that the specific or relative permeability of a magnetic substance is a number equal to  $\mu_1/\mu_0$ .

## APPENDIX V

*Modifications that might advantageously be introduced into certain classical magnetic formulae, in view of the International Convention recently recommended by the International Electrotechnical Commission in 1930-31.*

IN NON-MAGNETIC MEDIA, i.e. free space, a vacuum, or air assumed to be so nearly equivalent to a vacuum that its correction for magnetization may be ignored:

A. *Magnetomechanical Force*  $f$ , between two like poles, assumed as free point poles, each of strength  $m$  units, separated by a distance  $r$ , in a non-magnetic medium of space permeability  $\mu_0$ , the numerical value of which is unity in the classical c.g.s. magnetic system:

Revised Formula

$$f = \frac{m^2}{\mu_0 r^2}$$

instead of

Classical Formula

$$f = \frac{m^2}{r^2} \dots\dots(1).$$

B. *Intensity of Tractive Force*  $f'$  or *Tension/unit area* exerted across an air gap or *entrefer*, between opposed parallel plane polar surfaces, over which the uniform magnetic flux density is  $B$ :

$$f' = \frac{B^2}{8\pi\mu_0}$$

instead of

$$f' = \frac{B^2}{8\pi} \dots\dots(2).$$

C. *Magnetic Volume Energy*  $w$  in free space carrying uniform flux density  $B$  and magnetizing force  $H$ :

$$w = \frac{\mu_0 H^2}{8\pi} = \frac{HB}{8\pi} = \frac{B^2}{8\pi\mu_0}$$

instead of

$$w = \frac{H^2}{8\pi} = \frac{HB}{8\pi} = \frac{B^2}{8\pi} \dots\dots(3).$$

In each of the above cases, the numerical results will be the same with the revised formula as with the classical formula, so long as the classical c.g.s. magnetic system is used. With other systems, however, numerical values for  $\mu_0$  differing from unity must be used, except with the Maxwell q.e.s. system (Quadrant, Eleventh-gramme, Second). In the m.k.s. system (Metre, Kilogramme, Second) unrationalized,  $\mu_0 = 10^{-7}$ , and rationalized  $4\pi\mu_0 = 10^{-7}$ . In the c.g.s.s. system (Cm., Gramme-seven, Second) unrationalized,  $\mu_0 = 10^{-9}$ , and rationalized,  $\mu_0 = 4\pi \times 10^{-9}$ . It seems, therefore, desirable to retain the symbol  $\mu_0$  in every instance as generic.

IN MAGNETIC MEDIA.

D. *Formula for Uniform Magnetization*:

$$B = \mu H = \mu_0 H + 4\pi \mathcal{J} \quad \text{instead of} \quad B = H + 4\pi \mathcal{J} \dots\dots(4),$$

where  $\mathcal{J}$  is the uniform intensity of magnetization of the material.

$$\text{If } \mathcal{J} = 0, \quad B = \mu_0 H \text{ instead of } B = H \dots\dots(4a).$$

E. *Absolute Permeability of the Material*  $\mu$  (dividing equation (4) by  $H$ ):

$$\mu = \mu_0 + 4\pi \frac{\mathcal{J}}{H} = \mu_0 + 4\pi \kappa \quad \text{instead of} \quad \mu = 1 + 4\pi \kappa \dots\dots(5).$$

F. *Magnetic Susceptibility of the Material*  $\kappa$  (from last equation):

$$\frac{\mu - \mu_0}{4\pi} \quad \text{instead of} \quad \kappa = \frac{\mu - 1}{4\pi} \quad \dots (6).$$

## APPENDIX VI

### *The m.k.s. system*

In the early years of the present century Prof. Giovanni Giorgi, Professor of Mathematical Physics in the University of Palermo, pointed out the advantages which in his opinion made it desirable to accept the metre, the kilogramme and the second as fundamental mechanical units in place of the centimetre, the gramme and the second. He also called attention to the fact that if electrical quantities were to be included a fourth fundamental\* unit was necessary.

Prof. Giorgi described his system in various papers published in Italy in 1901 and 1902 and in a paper on "Rational Units of Electromagnetism" read before the Physical Society of London on May 23, 1902.

In a note to his paper reprinted from the *Electrical World* he writes: "I assume as fundamental the volt or the ampere, as arbitrarily chosen units and not depending from (*sic*) any mechanical unit." At a rather later date he indicated his preference for the ohm as the fourth unit, and in a paper submitted to the Electrical Congress at St Louis in September 1904 he writes: "As fundamental units of this system may be taken: the metre, the kilogramme, the second and the ohm (the latter to be defined by the practical standard adopted by the Congress of 1903 or by the standard kept by the Board of Trade in London)."

In more recent years this has come to be the International Ohm, i.e. the resistance at a temperature of 0° C. of a column of mercury 106.300 cm. in length having a mass of 14.4521 grammes†.

Meanwhile "The completion of the practical system of units" had been attracting attention elsewhere, and a letter having this title was published in the *Electrician*‡ by Prof. David Robertson of Bristol on April 22, 1904. From this the following quotations are taken: "Four fundamental quantities are really necessary for a system of electrical units, length, mass and time usually being three of them. In the electromagnetic system magnetic permeability is taken as the fourth, that of air being the arbitrary unit.

"But permeability is not the best quantity to take as fundamental since its accurate comparison is a matter of some difficulty. Electrical resistance can be accurately compared with comparative ease, and we have excellent material standards of resistance."

\* On Maxwell's electromagnetic system this fourth unit is secured by the assumption that the permeability of free space is unity, while on the electrostatic system the same object is attained by the assumption that the inductive capacity of air is unity.

† For a fuller account of Prof. Giorgi's system see *Nature*, April 21 and June 9, 1934, "The Giorgi (m.k.s.) System of Units."

‡ Taken by permission from the *Electrician*, April 22, 1904.

“By taking as the four fundamental or arbitrary units the metre, kilogramme, second and ohm (derived from a mercury or wire standard) we get a complete system which includes all the established practical electrical units and gives units which have a convenient magnitude for most purposes. Instead of resistance we may take electricity with the coulomb, defined from the electrolysis of silver, as the fundamental unit\*.”

In these units with the metre as the unit of length, the value of  $\mu_0$ , the magnetic permeability of air, is  $4\pi \times 10^{-7}$ , while that of  $\kappa_0$ , its inductive capacity, is  $1/(36\pi \times 10^9)$ .

The last suggestion has been revived lately by Prof. Cramp in a letter to *Nature*.

### III. CERTAIN THERMODYNAMIC SYMBOLS

At an early date Prof. Keesom submitted to the Commission certain proposals approved by the first Commission of the International Institute of Refrigeration, stating that the Institute wished to formulate its conclusions so as to be as nearly as possible in accord with the resolutions of the S.U.N. Commission. The Congress of Refrigeration also proposed the name Thermal Potential for Gibbs' Function. The question came before the British National Committee for Physics in the spring of 1933, and the conclusions reached were circulated to members of the S.U.N. Commission, in a table giving a résumé of the information received. In drawing up their suggestions the British Committee received valued help from Sir Alfred Ewing\* as to the practice of engineers.

The proposals were brought to the notice of the American Standards Association, and the Chairman of the Sub-Committee of that Association on Symbols for Heat and Thermodynamics has sent a letter setting forth the U.S. viewpoint on the matter.

A meeting of the British National Committee was held on July 26, 1934 to consider these various suggestions, and as a result some of their proposals of 1933 were modified.

Table 1 gives a summary of the information now before the S.U.N. Commission.

In a letter dated June 13, 1934, Dr Moss, Chairman of the Sub-Committee of the American Standards Association which has dealt with the matter points out that while  $E$  is used for Internal Energy by some British and some American authors other writers in both countries use  $U$ , which is the only letter used by Germans for this purpose.

For Free Energy the American symbol is  $\psi$  and this was also used in the earlier British proposals; this appears to Dr Moss to be a reason for retaining it, but in the more recent list the British proposal is  $F$ . The symbol  $\psi$  has been dropped.

For Gibbs' Function Dr Moss prefers  $\zeta$  or  $\varkappa$  to the letter  $G$ .

It should be noted that it is the American practice to use capitals for any weight and small letters when concerned only with unit weight.

To turn now to the British list. In their earlier proposal  $E$  was used as the symbol for Internal Energy; at the more recent meeting  $U$  was preferred but there was no strong feeling on the matter. From the information before the Committee  $U$  seemed the symbol most favoured, and the British Committee was willing to fall in with this; at the same time it was noted that  $E$  was used almost exclusively by English engineers, though the British Standards Institution recognize both  $E$  and  $U$ .

As to the four quantities  $U$ ,  $U-TS$ ,  $U-TS+PV$ ,  $U+PV$ , it was pointed out that they are all cognate and should be regarded as on a parity in the sense that they are all potentials, so that by suitable differentiations of each, any of them can yield

\* The Commission has learned with great regret of the death of Sir Alfred since the meeting.

the complete state of a substance, entropy or temperature, pressure or volume, thermoelectric current or e.m.f. For this reason it was felt that a standard notation would not adopt for them a series of unconnected letters and that it was desirable that all should come from the same fount. Roman capitals were preferred. Hence the proposal to use  $F$ ,  $G$ ,  $H$  for the last three.

It has also been suggested that if  $E$  be adopted for Internal Energy these four connected quantities will be denoted by the four consecutive letters  $E$ ,  $F$ ,  $G$ ,  $H$ .

Table 1. Thermodynamic symbols

	Entropy	Internal Energy	Free Energy $U - TS$	Gibbs' Function $U - TS + PV$	Heat Content or Enthalpy $U + PV$
<i>Standardizing Bodies</i>					
Fifth International Congress of Refrigeration (1928)	$S$	$U$	$F$		$I$ , $H$ or $W$
American Standards Association	$S$	$U$	$\psi$	$\zeta$ or $z$	$H$
British Standards Institution	$\phi$	$E$ or $U$	$\frac{F}{T}$	$G$	$\frac{H}{T}$
British National Committee for Physics	$S$	$U$	$F$	$G$	$H$
German Practice*	$S$	$U$	$F$	$H$	$I$
<i>Engineers</i>					
Callendar	$\phi$	$E$	—	$G$	$H$
Ewing	$\phi$	$E$	—	$G$	$I$
Zeuner	$P$	$U$	—	—	—
<i>Physicists</i>					
Clausius	$S$	$U$	$w$	—	—
Gibbs	$\eta$	$\epsilon$	$\psi$	$\zeta$	$\chi$
Hoare	$\phi$	$E$	$\psi$	$\zeta$	$\bar{H}$
Helmholtz	$S$	$U$	$F$ or $H$	—	$\phi$
Kelvin	$H/t$	$H$ , $Q$	—	—	—
Planck	$S$	$U$	$F$	$-T\phi$	$W$
<i>Chemists</i>					
Duhem	$S$	$U$	$F$	$\phi$	—
Guggenheim	$S$	$E$	$F$	$G$	$H$
Lewis and Randall	$S$	$E$	$A$	$F$	$H$
Nernst	$S$	$U$	$A$	—	—
Sackur	$S$	$E_v$	$F_v$	$F_v$	$E_p$
Schottky, Ulich and Wagner	$S$	$U$	$F$	$G$	$H$
Taylor	$S$	$U$	$A$	$G$	$H$

\* Information supplied by Prof. Wallot of the German A.E.F.

The symbols  $E$ ,  $F$ ,  $G$ ,  $H$  are used in Dr Guggenheim's *Modern Thermodynamics*. They have the following useful mnemonic characteristics,  $E$  Internal Energy,  $F$  Free Energy,  $G$  Gibbs' Function,  $H$  Total Heat.

The British Committee are also prepared to accept the name Thermal Potential for Gibbs' Function.

With regard to the use of  $\psi$  to represent Free Energy, it has been pointed out that this symbol, at least as a capital letter, is already used by Planck and others to represent the function  $S - U/T$ .

As to the choice of a symbol for entropy, stress was laid by Sir Alfred Ewing on



the use of  $\phi$ , by far the most frequent choice in earlier days. He pointed out that its use was almost universal in British physical as well as engineering textbooks and was the symbol originally given by Rankine to this function. While in Germany, and indeed elsewhere,  $S$  is used by chemical authors, still he claims that to drop  $\phi$  would be a serious departure from generally recognised English practice. It would be unreasonable, he feels, to expect chemists to drop  $S$ , but  $\phi$  should be an accepted alternative. He is also doubtful whether English engineers would be willing to drop  $E$  as an alternative to  $U$  for Internal Energy.

Sir Alfred Ewing also points out that the symbol  $I$  for Heat Content is common in English engineering books and that the use of  $I$  or  $i$  with this meaning is universal in Germany.

The information collected above has made it clear that there is no general agreement as to the symbols to be used for these quantities. At the same time the S.U.N. Commission is of opinion that it is desirable to make an effort to remedy the existing confusion and accordingly they recommend:

**I. That Table 2 be put forward for the National Committees as a satisfactory series of symbols and nomenclature for the thermodynamic quantities referred to, and**

**II. That  $E$ ,  $\phi$  and  $I$  be accepted as alternative symbols for Internal Energy, Entropy and Heat Content respectively.**

**III. That thermodynamic quantities should always be expressed in the Centigrade scale of temperature.**

Table 2. Symbols for Thermodynamic quantities  
(Recommended for general adoption)

Name	Entropy	Internal Energy	Free Energy	Thermal Potential or Gibbs' Function	Total Heat, Heat Content or Enthalpy	Work
Formula	—	—	$U - TS$	$U - TS + PV$	$U + PV$	
Symbol	$S$ or $\phi$	$U$ or $E$	$F$	$G$	$H$ or $I$	$W$

In the above formulae  $P$  and  $V$  should be interpreted as representing a generalized force and generalized co-ordinate respectively.

It is not suggested that changes should be made in the notation employed in existing books but it is hoped that in the future authors will as far as possible adopt the symbols included in Table 2.

## IV. THE FUTURE WORK OF THE S.U.N. COMMISSION

At the meeting of the International Union of Physics at Brussels when the S.U.N. Commission was set up it was pointed out that definitions of other standards besides those of the Standard Thermal Unit were desirable and the Commission has now dealt with standard symbols and nomenclature in certain branches of electromagnetism and of thermodynamics.

The question arises, what is to be its work in the immediate future? Can it usefully assist in other branches of physics, e.g. optics, acoustics, etc.? In quite a number of subjects there are now special international bodies which deal, among other matters, with the definitions and nomenclature of their subject; such are, for example, the International Commission on Illumination and the International Congress of Radiology.

It is clear that any steps the Union might desire to take towards defining terms in subjects already dealt with by an international body should be taken in close co-operation with that body. The Union would not usually wish to carry out an independent investigation into questions already examined by competent experts. Moreover, in a glossary of terms and definitions there is much that is necessarily technical and not of special interest to physicists as a body. In such a case as this the Union might invite the international body concerned to keep the S.U.N. Commission in touch while the work is in progress, and ask it to give consideration to suggestions made by the Commission with a view to rendering the result of value to physicists in general. On the completion of the list the S.U.N. Commission should take note of it and bring it to the notice of the Union and its adhering members.

In any case in which the Union decided to publish a list of terms already adopted officially by another international body, care should be taken to secure harmony between the two series of definitions. Such a case would arise whenever the official list contained definitions of terms in general use in physics; as an example of this there is given in Appendix I a series of definitions of the most important quantities used in photometry and illuminating engineering issued by the International Commission on Illumination.

Such a list might well find its place among the publications of the Union.

Again there are a number of subjects common to many branches of physics. Terms used to describe and define wave motion, for example, occur in electricity, optics, acoustics, aeronautics, etc., and definitions of these terms are to be found in glossaries compiled for each of these branches. The S.U.N. Commission could do useful work in bringing together these definitions and possibly issuing a list which might be accepted by all.

There is another group of subjects, acoustics, for example, for which there is at present no international association. Thus in acoustics the British Standards Institute is about to issue a very complete glossary while a Committee of the Acoustical Society of America dealing with standards has already issued a report the purpose of which is "to define the terms used in the various branches of acoustics in order to reduce the confusion which exists due to the use of a single term to represent different concepts and of several terms to represent the same concept."

In such a case as this where two or more reports covering the same ground exist, or two or more bodies are endeavouring to standardize the same subject, the S.U.N. Commission could do useful work in harmonizing the two. Its action at the present meeting in dealing with certain thermodynamical terms is an example of this.

It would appear, then, that there are at least three directions in which the S.U.N. Commission might usefully continue to work:

1. By co-operating with existing international bodies engaged in the preparation of glossaries or lists of definitions with a view to making them more useful to physicists in general.

2. By preparing for general adoption, lists of terms occurring in two or more branches of physics.

3. By assisting those who, in any country, are engaged in preparing such lists, with a view to bringing workers in different countries into contact and securing harmony in the results of their work.

As the work proceeds experience may reveal other similar directions in which the Commission can usefully help.

The Commission on Symbols, Units and Nomenclature therefore recommends:

**That the Commission on Symbols, Units and Nomenclature be authorized by the International Union of Pure and Applied Physics to continue its work on the lines indicated above.**

## APPENDIX I

### *Definitions and vocabulary in Photometry and Illuminating Engineering*

It should be noted that luminous flux is defined as follows: "The rate of passage of radiant energy evaluated by reference to the luminous sensation produced by it.

"Although luminous flux should be regarded, strictly, as the rate of passage of radiant energy as just defined, it can, nevertheless, be accepted as an entity for the purposes of practical photometry, since the rate of passage may be regarded as being constant under these conditions." It will be seen that the term "flux" is used here in a somewhat different sense from that ordinarily attached to it.

Further, the ratios  $\rho$ ,  $\alpha$  and  $\tau$  apply to material bodies or the surfaces of such

bodies and are defined as "the ratio of the flux reflected (absorbed, transmitted) by the body to the flux incident upon it."

Table

Quantity	Symbol	Unit	Defining equation
Luminous flux	$F$ or $\Phi$	Lumen	—
Luminous intensity	$I$	Candle	$I = dF/d\omega$
Illumination	$E$	Lux (phot. foot-candle)	$E = dF/ds$
Brightness	$B$	Candle per unit area	$B = dI/ds \cos \theta$
Radiance	$R$	Lumen per unit area	$R = dF/ds$
Quantity of light	$L$	Lumen-hour	$L = Ft$
Luminosity factor of radiation	$K$	—	—
Reflection factor	$\rho$	(Ratios)	
Absorption factor	$\alpha$		
Transmission factor	$\tau$		

$\omega$  = solid angle in radian measure.

$s$  = area.

$\theta$  = angle of emission.

It is probable that some of the present definitions will be amended and improved in the future, but it is almost certain that the significance attached to the above terms, and the symbols shown will remain unchanged as they are now used almost universally.

# V. NOTE SUR CE QUE POURRAIENT ÊTRE LES DÉFINITIONS DES GRANDEURS MAGNÉTIQUES

PAR HENRI ABRAHAM

Paris

## AVANT-PROPOS

LES définitions des grandeurs magnétiques ne sont pas encore établies d'une manière précise et universellement adoptée. L'accord est bien à peu près réalisé pour l'induction (vecteur  $B$ ), mais il n'en est pas de même pour ce que l'on a appelé le "vecteur  $H$ ," dont la définition reste très incertaine\*.

L'objet principal de la présente Note est d'esquisser une description générale des phénomènes magnétiques qui ne comporte que la conception en chaque point du champ d'une seule espèce de grandeur physique, l'induction magnétique.

Les définitions que nous présentons font du "vecteur  $B$ " et du "vecteur  $H$ " des grandeurs de même espèce: ce sont toutes deux des inductions. Dès lors, les noms de Gauss et d'Oersted qui ont été proposés pour les unités c.g.s. (électromagnétiques) de " $B$ " et de " $H$ " ne sont que deux noms différents donnés à une seule et même chose, l'unité c.g.s.m. d'induction magnétique.

Nous demandons que l'on veuille bien réfléchir aux définitions† présentées dans l'exposé qui va suivre, en nous excusant de la forme impérative que nous avons adoptée pour plus de clarté. Nous avons en général laissé de côté la démonstration des propositions que nous avançons: on trouvera ces démonstrations dans les notes annexes.

\* Chargé par la Commission des Unités de l'Union Internationale de Physique de préparer après enquête un Rapport sur ce que pourraient être les définitions des Grandeurs Magnétiques, je remercie sincèrement les physiciens et les techniciens de divers pays qui m'ont aidé dans cette tâche par leurs conseils et leurs critiques mais je dois un remerciement particulier à Monsieur Liénard pour les amicales et très utiles communications qu'il a bien voulu me faire sur sa manière de voir qui est suivie de près dans ce rapport.

† La définition des grandeurs physiques est une question essentiellement distincte de celle du choix des unités de mesure et de la constitution d'un système d'unités.

Chaque espèce de grandeur se mesure par des comparaisons avec une *unité intrinsèque*. Les comparaisons se font par l'application de règles d'égalité et d'addition qui sont conditionnées par les faits expérimentaux, et dont la spécification rentre dans la définition de la grandeur. Mais le choix de l'*unité intrinsèque* est entièrement libre; sa spécification et la constitution des systèmes d'unités résultent ensuite de *conventions*, auxquelles on ne demande que de ne pas comporter de contradictions.

Désireux de séparer nettement ces questions, et d'obtenir des formules qui fussent bonnes pour tous les systèmes d'unités, nous ne nous sommes pas imposé de règles de coordination entre les unités magnétiques, laissant ainsi ces unités indépendantes. Nous avons donc introduit dans l'expression algébrique des lois expérimentales une série de coefficients numériques  $\alpha$ ,  $\beta$ ,  $\gamma$ ,... dont les valeurs peuvent être fixées ultérieurement quand on précise les règles de coordination propres à chaque système d'unités.

Toutefois, dans un but de simplification nous avons adopté dès le début pour les unités mécaniques les conventions de coordination habituelles.

# I. INTRODUCTION. LES THÉORIES DU MAGNÉTISME

La définition des grandeurs magnétiques ne présente pas de difficultés réelles dans le cas des champs magnétiques créés dans le vide (ou, pratiquement, dans l'air).

Pour savoir ce qui se passe dans les corps aimantés, à l'intérieur desquels on ne peut pas pénétrer, on est réduit dans toutes les théories à des considérations conjecturales.

Dans l'ancienne théorie du magnétisme, on admettait l'existence dans les corps aimantés de masses positives et négatives, ou tout au moins de doublets d'une matière attirante, qui était supposée agir suivant une loi d'inverse carré de la distance.

Malgré les services qu'elle a rendus, cette théorie ne saurait être conservée parce qu'elle est en contradiction avec les faits en ce qui concerne le degré de dissymétrie des champs magnétiques. L'hypothèse des masses attirantes entraîne en effet, par exemple, qu'un champ magnétique de révolution doit être symétrique par rapport à chaque plan méridien, alors que les phénomènes de polarisation rotatoire et les rotations continues des courants électriques dans les champs magnétiques de révolution montrent que cette symétrie n'existe pas : le degré de symétrie locale d'un champ magnétique est celui d'un cylindre de révolution tournant sur lui-même et non pas celui du cylindre immobile à quoi conduisait l'hypothèse des masses magnétiques.

L'hypothèse des courants particuliers d'Ampère, au contraire, est conforme à ce que l'expérience montre être le degré de dissymétrie du champ magnétique.

Cette conception des courants particuliers, vers laquelle les théories modernes sur la constitution de la matière sont nettement orientées, entraîne aussi de grandes simplifications.

Dans cette hypothèse, les seules lois d'actions à distance que nous puissions envisager sont les lois d'action *dans le vide*.

Il ne peut plus être question de lois d'action magnétique comportant un coefficient d'attraction *dépendant du milieu extérieur*. Cette dernière conception, qui ne s'appuyait sur aucun fait d'expérience, paraît bien aujourd'hui être à peu près abandonnée, mais elle a pesé pendant longtemps de la manière la plus fâcheuse sur l'enseignement de l'électromagnétisme.

Ce sera donc à l'hypothèse d'Ampère que nous nous adresserons quand, après avoir défini les grandeurs magnétiques pour le vide, nous chercherons comment ces définitions doivent être étendues pour l'intérieur des corps magnétiques. Mais nous pouvons dès maintenant déduire une conséquence importante de l'hypothèse d'Ampère.

S'il est vrai que les aimants sont des assemblages de courants, ce seront les mêmes causes qui pourront agir sur des courants et sur des aimants; et si, comme nous allons le faire, nous pouvons attribuer les forces exercées sur les courants aux actions locales de ce que nous appellerons l'induction magnétique, ce devra être aussi cette induction magnétique qui agira sur les aimants. Il n'y a donc pas à imaginer une autre grandeur magnétique locale distincte de l'induction, pour lui conférer le monopole de l'action sur les aimants.

## II. DÉFINITION DE L'INDUCTION MAGNÉTIQUE

Nous nous occupons d'abord des champs créés dans le vide, ou pratiquement dans l'air, par des aimants ou des courants permanents.

Dans ces champs magnétiques, on constate qu'en un même lieu il y a exacte proportionnalité entre divers phénomènes: action sur un aimant, action sur un courant, polarisation rotatoire dans un corps non-magnétique, forces électromotrices induites, etc. et ces effets sont aussi proportionnels à l'intensité des courants qui produisent le champ, ainsi qu'à l'intensité des courants à l'aide desquels on peut compenser (détruire) le champ magnétique.

En présence de cet ensemble de faits expérimentaux, on est conduit à concevoir, en chaque point du champ, l'existence d'une grandeur physique, cause immédiate de toutes ces manifestations magnétiques, qui lui seraient directement proportionnelles. C'est une grandeur orientée ayant le degré de symétrie du cylindre de révolution qui tourne sur lui-même.

La définition de cette grandeur, que nous appellerons induction magnétique se complète par les règles de comparaison par égalité et addition: ces règles consistent à constater qu'il y a égalité ou addition pour l'un quelconque des effets que nous signalons, ou pour les courants producteurs ou compensateurs du champ.

Les diverses définitions auxquelles on arrive ainsi suivant l'élément de comparaison que l'on emploie, sont toutes rigoureusement équivalentes et définissent la même grandeur physique en raison des lois expérimentales de proportionnalité et d'additivité que nous connaissons.

Bien que l'induction magnétique n'ait pas le degré de symétrie d'une demi-droite, et ne soit représentée qu'imparfaitement par un tel élément géométrique, cette représentation vectorielle est néanmoins très utile: elle nous donne, pour le vide, la définition du *vecteur*  $\mathbf{B}$ .

Rappelons maintenant quelques lois expérimentales.

Dans le champ d'un courant permanent  $\mathbf{I}$ , l'induction  $\mathbf{B}$  que nous venons de définir dérive d'un potentiel, et son intégrale de ligne  $\oint (\mathbf{B}, d\mathbf{l})^*$  est en général nulle, excepté quand le contour d'intégration s'entrelace avec le courant. Dans ce cas on doit écrire  $\oint (\mathbf{B}, d\mathbf{l}) = \alpha \mathbf{I}$ , la constante  $\alpha$  dépendant du choix des unités adoptées pour le courant électrique et pour l'induction  $\mathbf{B}$ —et l'expression générale du potentiel de  $\mathbf{B}$  est  $\mathbf{P} = \frac{\alpha}{4\pi} \Omega \mathbf{I}$ , en désignant par  $\Omega$  l'angle solide sous lequel on voit le courant. Il y a enfin l'additivité des potentiels  $\mathbf{P}$  pour les ensembles de courants.

Le vecteur  $\mathbf{B}$  est, aussi, conservatif: le flux d'induction au travers d'une surface fermée ( $\Phi = \iint \mathbf{B}_N \cdot d\mathbf{s}$ ) est nul, ce que l'on peut représenter par la notation:

$$\text{div. } \mathbf{B} \equiv \frac{\partial \mathbf{B}_x}{\partial x} + \frac{\partial \mathbf{B}_y}{\partial y} + \frac{\partial \mathbf{B}_z}{\partial z} = 0.$$

La force exercée sur un élément de courant mobile, placé dans le vide en un lieu où l'induction est  $\mathbf{B}$ , est proportionnelle au produit vectoriel de l'induction et du courant élémentaire. La valeur numérique de cette force dépend des unités

\* La virgule signifie le produit scalaire des deux vecteurs enfermés entre les parenthèses ( ).

adoptées pour le courant et l'induction, et nous devons écrire la formule correspondante,  $\mathbf{F} = \beta [\mathbf{B} \cdot \mathbf{Id}l]$ , en introduisant un nouveau facteur numérique  $\beta$  lié aux choix d'unités.

L'expérience montre par ailleurs que la valeur numérique des forces électromotrices induites est donnée par la formule  $E = -\beta \frac{d\phi}{dt}$ , et le rapprochement de ces deux dernières égalités expérimentales où figure le même coefficient  $\beta$  fournit une précieuse confirmation du principe de la conservation de l'énergie.

### III. MOMENTS MAGNÉTIQUES. INTENSITÉ D'AIMANTATION

A grande distance, le champ créé par un courant est indépendant des détails de forme du courant: il est entièrement défini quand on se donne le *vecteur SI* dont les composantes sont numériquement égales aux produits de la mesure de l'intensité du courant par celles des surfaces projections du circuit sur les plans de coordonnées.

Le potentiel de l'induction est alors donné par la formule

$$P = \frac{\alpha}{4\pi} \frac{\mathbf{SI} \cos \theta}{r^2}$$

( $\theta$  étant l'angle du vecteur  $\mathbf{SI}$  et du rayon  $r$ ).

Il aurait été naturel de convenir que dans tout système d'unités magnétiques, le *vecteur SI* représenterait le *moment magnétique* du courant et que l'on écrirait:

$$\mathbf{M} = \mathbf{SI}.$$

Mais cette convention n'a pas été faite dans tous les systèmes d'unités. Pour pouvoir écrire ici des formules valables pour tous ces systèmes, il nous faut donc laisser indéterminée l'unité de moment magnétique et écrire:

$$\mathbf{M} = \gamma (\mathbf{SI})$$

en introduisant une nouvelle constante numérique  $\gamma$  qui n'aura pas nécessairement la même valeur dans tous les systèmes d'unités qui ont été effectivement constitués.

D'après les lois d'additivité, le moment magnétique d'un ensemble de courants rassemblés dans un espace restreint sera alors:

$$\mathbf{M} = \gamma \Sigma (\mathbf{SI}).$$

Pour un aimant enfin, qui est un assemblage de courants, le moment magnétique sera encore:

$$\mathbf{M} = \gamma \Sigma (\mathbf{SI}).$$

D'après cela, et inversement, quand un courant, un groupe de courants ou un aimant\* de moment magnétique  $\mathbf{M}$  est placé dans un champ pratique-

\* Dans l'ancienne théorie du magnétisme, on parlait d'une loi d'attraction du type

$$F = \delta \frac{mm'}{r^2}$$

en posant pour les moments magnétiques  $\mathbf{M} = m.l$ .

Il est aisé d'établir (voir la 1<sup>re</sup> Note Annexe) que les constantes  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  sont nécessairement liées par la condition:

$$\alpha\beta = 4\pi\gamma^2\delta$$

en raison de l'équivalence des courants et des aimants.



ment uniforme où l'induction est  $\mathbf{B}$ , il est soumis à un couple  $C$  dont la valeur est:

$$C = \frac{\beta}{\gamma} [\mathbf{B} \cdot \mathbf{M}] \text{ (produit vectoriel).}$$

*Intensité d'aimantation.* On donne toujours ce nom au moment magnétique par unité de volume. Nous représenterons cette quantité par la lettre  $\mathbf{A}$ , et nous écrirons

$$\mathbf{A} = \frac{\mathbf{M}}{V} \text{ ou } \mathbf{A} = \frac{d\mathbf{M}}{dv}.$$

En nous rappelant la définition du moment magnétique, nous aurons donc pour un corps aimanté:

$$\mathbf{A} = \gamma \frac{\sum \mathbf{SI}}{v} \text{ ou } \mathbf{A} = \gamma (\mathbf{SI})_{\text{moyen}}.$$

#### IV. DÉFINITION DES GRANDEURS MAGNÉTIQUES POUR L'INTÉRIEUR DES CORPS AIMANTÉS

Dans l'intérieur des corps non-magnétiques ou des corps magnétiques non-aimantés, les courants particuliers n'ont pas entre eux de coordination, ils sont distribués d'une manière désordonnée, en sorte que leurs effets se détruisent en moyenne: le champ magnétique intérieur moyen est alors, sans modifications, celui qui est créé directement, comme dans le vide, par les causes extérieures, malgré qu'il s'y superpose le champ des courants particuliers, parce que ce dernier champ magnétique est nul en moyenne.

Il n'en est plus de même si les courants particuliers ont une certaine coordination. Nous pouvons alors envisager autour de chaque point une valeur moyenne de l'induction, malgré les variations rapides de cette induction au voisinage de chaque courant particulier. L'intensité d'aimantation autour de chaque point peut aussi être définie, et ces deux quantités, *induction moyenne* et *intensité d'aimantation*, ont des variations lentes et continues d'un point à l'autre du champ.

L'*induction moyenne* est donnée par la formule vectorielle

$$\mathbf{B}_2 = \frac{1}{V} \iiint \mathbf{B} \cdot dv,$$

dans laquelle nous employons la notation  $\mathbf{B}_2$  pour distinguer l'induction moyenne de l'induction *vraie*  $\mathbf{B}$ . L'intégration de  $\mathbf{B}$  est étendue à un volume  $V$  entourant le point étudié. Ce volume  $V$  doit être considéré comme très petit, tout en étant assez grand pour renfermer beaucoup de courants particuliers.

En étudiant la formation de ces moyennes, on peut établir une série de propositions importantes, que nous allons énumérer (voir 2<sup>e</sup> et 3<sup>e</sup> Notes Annexes).

(i) L'induction moyenne peut être décomposée en deux parties, dont la première ne dépend que de l'intensité d'aimantation locale,  $\mathbf{A}$ , et a pour valeur  $\alpha \mathbf{A} / \gamma$ . L'autre partie est une induction complémentaire, que l'on aurait quelques raisons

d'appeler *induction magnétisante*, et que nous représenterons par la notation  $\mathbf{B}_0$ , en écrivant :

$$\mathbf{B}_2 = \alpha \mathbf{A} / \gamma + \mathbf{B}_0.$$

(ii) A l'extérieur des corps magnétiques, là où l'intensité d'aimantation est nulle, les inductions  $\mathbf{B}_2$  et  $\mathbf{B}_0$  se confondent toutes deux indistinctement avec l'induction vraie  $\mathbf{B}$ .

(iii) L'induction  $\mathbf{B}_0$  est ainsi définie dans tout l'espace. Elle dérive d'un potentiel, avec la condition  $\oint (\mathbf{B}_0, d\mathbf{l}) = \alpha I$  lorsque le contour d'intégration tourne autour d'un courant  $I$ .

Il en est de même pour l'induction vraie, mais non pour l'induction moyenne  $\mathbf{B}_2$  qui, en général, n'admet pas de potentiel.

(iv) Le potentiel de la partie de l'induction  $\mathbf{B}_0$  qui est créée par les courants particuliers est égal au potentiel des attractions d'une matière attirante fictive agissant suivant une loi d'attraction  $F = mm'/r^2$ , qui aurait en chaque point intérieur à l'aimant une densité cubique :

$$\rho = - \frac{\alpha}{4\pi\gamma} \operatorname{div} \mathbf{A},$$

tandis que la surface limite de l'aimant porterait une densité superficielle :

$$\sigma = \alpha \cdot \mathbf{A}_N / 4\pi\gamma.$$

(v) Si l'on calcule l'induction moyenne à l'intérieur d'un petit cylindre allongé dans le sens de l'aimantation, on trouve que le terme local  $\alpha \mathbf{A} / \gamma$  est l'induction moyenne créée dans ce cylindre par les courants particuliers qui y sont contenus, tandis que  $\mathbf{B}_0$  est l'induction due aux courants finis et aux courants particuliers extérieurs à ce cylindre.

(vi) L'induction moyenne  $\mathbf{B}_2$  est un vecteur conservatif, et les flux d'induction moyenne peuvent être substitués aux flux d'induction vraie dans le calcul des forces électromotrices induites.

(vii) Aux surfaces de discontinuités, la composante normale de l'induction moyenne  $\mathbf{B}_2$  et la composante tangentielle de l'induction magnétisante  $\mathbf{B}_0$  ne subissent pas de discontinuité, tandis que la discontinuité de l'intensité d'aimantation se reporte sur les autres composantes.

(viii) Dans l'expression  $C = \beta / \gamma (\mathbf{B} \cdot \mathbf{M})$  du couple résultant des forces exercées dans un champ uniforme sur une aiguille aimantée ayant un moment magnétique  $\mathbf{M}$ , on peut introduire indifféremment soit l'induction qui existe dans le champ extérieur donné, soit l'induction moyenne ( $\mathbf{B}_2$ ), évaluée pour l'intérieur de l'aiguille aimantée, telle qu'elle est conditionnée par le champ ambiant et par l'aimantation de cette aiguille.

## V. DÉFINITION DU "VECTEUR $\mathbf{B}$ " ET DU "VECTEUR $\mathbf{H}$ "

Nous nous trouvons maintenant avoir défini dans tout l'espace deux inductions,  $\mathbf{B}_2$  et  $\mathbf{B}_0$ , qui, confondues dans le vide extérieur, se séparent dans l'intérieur des corps magnétiques, et qui possèdent les propriétés que nous venons de rappeler.

Or ces propriétés sont, indistinctement et sans exception, celles-là mêmes par lesquelles on entend caractériser le "vecteur  $\mathbf{B}$ " et le "vecteur  $\mathbf{H}$ ." Nous sommes donc en droit de poser les définitions suivantes:

*La grandeur physique que l'on appelle le vecteur  $\mathbf{B}$ , n'est autre que l'induction magnétique  $\mathbf{B}$  définie sans ambiguïté dans le vide, et prolongée dans l'intérieur des corps magnétiques par l'induction moyenne  $\mathbf{B}_2$ . La grandeur physique que l'on appelle le vecteur  $\mathbf{H}$ , n'est autre que l'induction magnétique  $\mathbf{B}$  définie sans ambiguïté dans le vide, et prolongée dans l'intérieur des corps magnétiques par l'induction (magnétisante)  $\mathbf{B}_0$ .*

Nous ferons encore observer, en terminant, que tout ce qui précède est relatif aux grandeurs physiques elles-mêmes, sans préoccupation de leurs unités de mesures dont le choix reste entièrement libre.

#### En résumé

L'exposé qui précède fait apparaître  $\mathbf{B}$  et  $\mathbf{H}$  comme des grandeurs de même espèce.

Dans les systèmes d'unités dits électromagnétiques, et en particulier dans le système c.g.s.m., ces deux inductions sont mesurées avec la même unité.

Le Gauss et l'Oersted, que l'on a proposé d'employer comme unités distinctes pour la mesure de  $\mathbf{B}$  et de  $\mathbf{H}$ , sont ainsi une seule et même chose, l'unité c.g.s.m. d'induction magnétique à laquelle on a donné successivement deux noms différents.

### NOTES ANNEXES

#### NOTE I. RELATION ENTRE LES CONSTANTES $\alpha$ , $\beta$ , $\gamma$ , $\delta$

Cette relation peut être obtenue en identifiant les expressions d'une même force dans les deux notations. Prenons par exemple le cas de deux aimants de moments magnétiques  $\mathbf{M}$  et  $\mathbf{M}'$  centrés sur  $OZ$ , séparés par une distance  $r$  et parallèles respectivement à  $OX$  et  $OY$ . Le couple exercé sur l'un d'eux a pour valeur:

$$C = \frac{\alpha\beta}{4\pi\gamma^2} \frac{\mathbf{M}\mathbf{M}'}{r^3}.$$

Dans l'ancienne théorie, on aurait écrit:

$$C = \delta \mathbf{M}\mathbf{M}'$$

On doit donc bien avoir la relation:

$$\alpha\beta = 4\pi \cdot \gamma^2 \cdot \delta.$$

#### NOTE II. LES INDUCTIONS $\mathbf{B}$ , $\mathbf{B}_2$ ET $\mathbf{B}_0$ DANS L'INTÉRIEUR DES CORPS MAGNÉTIQUES

Le magnétisme étant dû aux courants particuliers qui agissent suivant les mêmes lois que les courants finis dans le vide, la valeur de l'induction magnétique vraie  $\mathbf{B}$  est définie sans ambiguïté en tout point du champ, à l'intérieur ou à l'extérieur des corps magnétiques.

C'est l'insuffisance de nos moyens d'observation qui nous conduit à envisager les moyennes que vont être l'intensité d'aimantation  $\mathbf{A}$  et l'induction magnétique moyenne  $\mathbf{B}_2$ .

Ces deux quantités se définissent par les formules vectorielles:

$$\mathbf{A} = \frac{1}{V} \gamma \Sigma (\mathbf{SI}) \quad \text{ou} \quad \mathbf{A} = \gamma (\mathbf{SI})_{\text{moyen}} \quad \text{et} \quad \mathbf{B}_2 = \mathbf{B}_{\text{moyen}} = \frac{1}{V} \left[ \int \mathbf{B} \cdot d\mathbf{v} \right].$$

Nous allons montrer comment le calcul de l'induction moyenne  $\mathbf{B}_2$  fait intervenir l'intensité d'aimantation locale  $\mathbf{A}$  et conduit à envisager une seconde induction moyenne,  $\mathbf{B}_0$ , que nous aurions quelques raisons d'appeler *induction magnétisante*.

Chaque élément de volume  $d\mathbf{v}$  contient un grand nombre de courants particuliers, mais comme nous supposons que l'intensité d'aimantation varie lentement d'un point à l'autre, nous pouvons substituer à ces divers courants un (ou plusieurs) courants plans orientés perpendiculairement à la direction de l'intensité d'aimantation, que nous prendrons comme direction de l'axe des  $Z$ .

Considérons maintenant un volume  $V$  que, pour simplifier, nous supposons symétrique par rapport à deux plans parallèles à  $ZOX$  et à  $ZOY$ , et cherchons d'abord la valeur moyenne de l'induction vraie,  $\mathbf{B}$ , qui serait créée aux divers points de ce volume  $V$  par les seuls courants particuliers qu'il contient. Nous admettons que ce volume  $V$ , qui renferme un très grand nombre de courants élémentaires, est néanmoins assez petit pour que l'intensité d'aimantation  $\mathbf{y}$  soit pratiquement uniforme.

En raison de la symétrie du volume  $V$ , les composantes suivant  $OX$  et  $OY$  ont des moyennes nulles, et la valeur moyenne  $\mathbf{B}_2$  de l'induction  $\mathbf{B}$  se confond avec la valeur moyenne de sa composante suivant  $OZ$ .

L'induction vraie  $\mathbf{B}$  dérive du potentiel

$$P = \frac{\alpha}{4\pi} \Sigma \mathbf{I} \Omega.$$

L'induction moyenne  $\mathbf{B}_2$  a donc pour valeur\*

$$\mathbf{B}_2 = \frac{1}{V} \iiint \mathbf{B}_z \, dx \cdot dy \cdot dz = \frac{1}{V} \iint dx \cdot dy \cdot \left[ \frac{\partial P}{\partial z} \right] dz = \frac{1}{V} (P_1 - P_2) \, dx \cdot dy,$$

expression dans laquelle  $P_1 - P_2$  est la différence de potentiel entre les deux points (1) et (2) où le cylindre élémentaire  $dx \cdot dy$  perce la surface limite. La valeur générale de cette différence serait

$$\frac{\alpha}{4\pi} \mathbf{I} (\Omega_1 - \Omega_2),$$

mais il faut y ajouter  $\alpha \mathbf{I}$  chaque fois qu'un cylindre élémentaire traverse le contour d'un courant particulier  $\mathbf{I}$ .

A eux seuls, ces termes supplémentaires  $\frac{1}{V} \iint \alpha \mathbf{I} \, dx \cdot dy$  fournissent à l'induction moyenne  $\mathbf{B}_2$  la contribution  $\frac{1}{V} \alpha \Sigma (\mathbf{SI})$  que nous pouvons écrire  $\alpha \mathbf{A} / \gamma$  en faisant apparaître l'intensité d'aimantation  $\mathbf{A}$ .

\* Lehfelddt, *Phil. Mag.*, 17, 275 (1909).

Le reste de l'intégrale fournit une autre contribution qui vaut

$$\mathbf{B}_1 = \frac{1}{V} \iiint \frac{\alpha}{4\pi} \Sigma \mathbf{IS} \cos \theta \cdot \cos \phi \cdot ds/r^2.$$

Dans cette expression que nous désignons par  $\mathbf{B}_1$ , les angles  $\theta$  et  $\phi$  sont ceux que font avec l'axe  $OZ$ , d'une part la normale à la surface limite sur l'élément  $ds$ , et d'autre part la droite de longueur  $r$  qui joint cet élément de surface au courant particulière ( $\mathbf{SI}$ ).

Mais nous pouvons remarquer que chacun des éléments de l'intégrale  $\mathbf{B}_1$  peut aussi être considéré comme représentant la composante suivant  $OZ$  du champ de gravitation que l'on obtiendrait à l'endroit où se trouve le courant ( $\mathbf{SI}$ ) si l'on avait répandu sur la surface limite une matière attirante fictive agissant suivant une loi d'attraction  $F = mm'/r^2$ , et dont la densité superficielle serait la composante, normale à la surface d'intégration, d'un vecteur  $\alpha \mathbf{IS}/4\pi$  orienté suivant  $OZ$ , c'est à dire suivant l'intensité d'aimantation.

En totalisant à la fois pour tous les courants ( $\mathbf{SI}$ ) et pour toute la surface qui limite le volume  $V$ , nous voyons que l'intégrale  $\mathbf{B}_1$  représente le champ d'attraction moyen dans le volume  $V$ , de la matière fictive répartie sur la surface limite avec la densité superficielle  $\sigma = \frac{\alpha}{4\pi\gamma} \mathbf{A}_N$  égale à la composante normale  $\mathbf{A}_N$  de l'intensité d'aimantation, multipliée par le coefficient  $\alpha/4\pi\gamma$  qui dépend du choix des unités.

En définitive :

*L'induction moyenne créée à l'intérieur du volume  $V$  par les courants particuliers qui y sont contenus est égale à la quantité  $\alpha \mathbf{A}/\gamma$  augmentée de la valeur de l'intégrale  $\mathbf{B}_1$  que nous venons de calculer.*

Il nous reste maintenant à compléter ce premier résultat en évaluant la valeur moyenne dans le même volume  $V$ , de l'induction créée en chaque point par les courants finis et par ceux des courants particuliers extérieurs à ce volume.

En partant de la valeur  $P = \frac{\alpha}{4\pi} \frac{\mathbf{IS} \cdot \cos \theta}{r^2}$  du potentiel d'un courant particulière ( $\mathbf{SI}$ ) et en procédant à une intégration par parties (suivant un calcul classique de l'ancienne théorie des masses magnétiques), nous verrons sans difficulté que l'induction produite en un point intérieur au volume  $V$  par les courants particuliers extérieurs à ce volume peut être représentée par le champ d'attraction en ce point d'une matière attirante fictive agissant suivant la loi  $F = mm'/r^2$  et qui serait répandue, d'une part dans la masse des corps aimantés avec une densité cubique  $\rho = -\alpha \operatorname{div} \mathbf{A}/4\pi\gamma$ , et, d'autre part sur toutes les surfaces limites, y compris la surface qui limite le volume  $V$ , avec une densité superficielle  $\sigma$  égale à la composante normale de l'intensité d'aimantation (multipliée par la constante  $\alpha/4\pi\gamma$ ).

En tenant compte du changement de sens de la normale, nous voyons que l'induction moyenne dans  $V$ , due aux courants extérieurs, a pour valeur l'intégrale  $\mathbf{B}_1$  de tout à l'heure, changée de signe, augmentée d'une certaine induction que nous appellerons  $\mathbf{B}_0$  et dont nous pouvons dire qu'elle comprend d'abord l'induction moyenne créée dans le volume  $V$  par les courants finis (qui ne sont pas en-

core intervenus) et en outre une certaine induction représentée par le champ d'attraction moyen des densités cubiques  $\rho$  et des densités superficielles  $\sigma$  de matière attirante fictive répandues dans la masse des aimants et sur leurs surfaces limites.

Si nous rassemblons maintenant les résultats de ces divers calculs nous pouvons écrire pour l'induction moyenne  $\mathbf{B}_2$  créée par les courants particuliers intérieurs au volume  $V$ :

$$\mathbf{B}_2 = \frac{\alpha}{\gamma} \mathbf{A} + \mathbf{B}_1 \quad \text{.....(1)}$$

et ensuite, pour le reste de l'induction vraie, qui provient des courants extérieurs :

$$-\mathbf{B}_1 + \mathbf{B}_0 \quad \text{.....(2).}$$

Nous obtenons ainsi la formule importante

$$\mathbf{B}_2 = \alpha \mathbf{A}_0 / \gamma + \mathbf{B}_0$$

qui relie l'induction moyenne  $\mathbf{B}_2$  en un point d'un corps magnétique avec l'intensité d'aimantation locale  $\mathbf{A}$  et avec l'induction  $\mathbf{B}_0$  que nous venons de définir.

#### NOTE III. LES PROPRIÉTÉS DES INDUCTIONS $\mathbf{B}_2$ ET $\mathbf{B}_0$

(1) L'induction  $\mathbf{B}_0$  dérive d'un potentiel avec la condition  $\int(\mathbf{B}_0, d\mathbf{l}) = \alpha \mathbf{I}$ .

En effet, la partie de  $\mathbf{B}_0$  qui provient des courants finis satisfait à ces conditions; et l'autre partie, qui est représentée par un champ de gravitation, dérive d'un potentiel *uniforme* pour lequel on a dans tout l'espace  $\int(\mathbf{B}, d\mathbf{l}) = 0$ .

(2) Si l'on calcule l'induction moyenne  $\mathbf{B}_2$  pour le volume d'un petit cylindre allongé dans le sens de l'aimantation, le terme local  $\alpha \mathbf{A} / \gamma$  est exactement égal à l'induction moyenne créée par les courants particuliers contenus dans le cylindre; et le terme  $\mathbf{B}_0$  est exactement égal à l'induction moyenne créée par les courants, finis et particuliers, situés à l'extérieur.

Cela tient à ce que les densités superficielles  $\sigma$  de matière attirante fictive n'existent que sur les très petites bases du cylindre et n'ont pas d'action appréciable.

(3) Si l'on admet, comme le disait Ampère, que les courants particuliers sont groupés en *petits solénoïdes*, le terme local  $\alpha \mathbf{A} / \gamma$  de l'induction moyenne  $\mathbf{B}_2$  représente exactement la contribution apportée par les inductions qui existent à l'intérieur des petits solénoïdes. Dès lors l'induction  $\mathbf{B}_0$  n'est autre que la valeur moyenne de l'induction vraie *dans la portion de l'espace qui n'est pas occupée par les solénoïdes particuliers*.

Cette remarque justifierait, dans l'hypothèse que nous venons d'introduire, que l'on donnât le nom d'*induction magnétisante* à l'induction  $\mathbf{B}_0$ , puisque c'est seulement dans les portions libres de l'espace que peut se trouver un solénoïde d'Ampère quand il subit l'action *magnétisante* de l'*induction vraie* qui le modifie ou l'oriente.

(4) Dans l'hypothèse où l'on nierait l'existence des courants particuliers, en disant que les particules magnétiques sont, non pas des courants, mais des *petits*

*aimants* droits de nature inconnue, tous les calculs que nous avons faits conserveraient leur valeur, en considérant seulement comme une loi expérimentale que le flux d'induction qui traverse un barreau droit uniformément aimanté est le même que pour le solénoïde équivalent.

(5) L'induction moyenne  $\mathbf{B}_2$  est un vecteur conservatif, sa *divergence* est nulle.

La relation fondamentale  $\mathbf{B}_2 = \alpha \mathbf{A} / \gamma + \mathbf{B}_0$  donne en effet :

$$\text{div. } \mathbf{B}_2 = \alpha \text{ div. } \mathbf{A} / \gamma + \text{div. } \mathbf{B}_0,$$

mais, d'après la signification de  $\mathbf{B}_0$ , l'équation de Poisson, relative aux attractions des densités cubiques  $\rho = -\alpha \text{ div. } \mathbf{A} / 4\pi\gamma$ , nous permet d'écrire :

$$\text{div. } \mathbf{B}_0 = 4\pi\rho = -\alpha \text{ div. } \mathbf{A} / \gamma.$$

Il en résulte bien que la divergence de  $\mathbf{B}_2$  est nulle.

(6) La condition  $\text{div. } \mathbf{B}_2 = 0$  entraîne que la composante normale de ce vecteur varie d'une manière continue aux surfaces de discontinuités.

D'autre part, sur ces surfaces l'action des densités superficielles fictives  $\sigma$  ne se fait sentir que sur la composante normale de  $\mathbf{B}_0$  ; la composante tangentielle de  $\mathbf{B}_0$  varie donc aussi d'une manière continue.

(7) Les deux expressions que l'on peut être tenté d'attribuer au couple exercé par un champ uniforme sur une aiguille aimantée, savoir :

$$C = \frac{\beta}{\gamma} [\mathbf{B}_2 \cdot \mathbf{M}] \quad \text{ou} \quad C = \frac{\beta}{\gamma} [\mathbf{B}_0 \cdot \mathbf{M}],$$

sont rigoureusement équivalentes puisque l'on a  $\mathbf{B}_2 = \alpha \mathbf{A} / \gamma + \mathbf{B}_0$ , avec  $\mathbf{M} = \mathbf{A} \cdot V$  et que le produit vectoriel  $[\mathbf{A} \cdot \mathbf{M}] = V [\mathbf{A} \cdot \mathbf{A}]$  est indemment nul.

#### NOTE IV. SUR LES SYSTÈMES D'UNITÉS ÉLECTROSTATIQUES ET SUR QUELQUES AUTRES SYSTÈMES D'UNITÉS

Les systèmes d'unités c.g.s. électrostatique et électromagnétique sont deux cas particuliers dans un groupe de systèmes à quatre unités indépendantes où les conventions de coordination d'unités consistent à donner la forme suivante\* aux égalités représentant les lois expérimentales de l'électromagnétisme :

Attractions magnétiques :	$F = \frac{mm'}{\mu_0 r^2}$
Moment magnétique d'un aimant :	$\mathbf{M} = m \cdot l$
Moment magnétique du courant équivalent :	$\mathbf{M} = \mu_0 (\mathbf{SI})$
Intensité d'aimantation :	$\mathbf{A} = \frac{d\mathbf{M}}{dV}$
Potentiel magnétique :	$\int (\mathbf{H}, d\mathbf{l}) = 4\pi\mathbf{I}$
Force électromotrice induite :	$E = - \frac{d}{dt} \mathbf{B}_N \cdot d\mathbf{s}$
Force sur un élément de courant :	$F = [\mathbf{B} \cdot \mathbf{Idl}]$
Couple sur un courant fermé :	$C = [\mathbf{B} \cdot \mathbf{SI}]$
Couple sur un aimant :	$C = [\mathbf{H} \cdot \mathbf{M}]$
Induction magnétique dans un aimant :	$B = \mu_0 \mathbf{H} + 4\pi\mathbf{A}$

\* Les crochets [...] indiquent des produits vectoriels.

Il n'est pas sans intérêt de montrer par quelle suite de *conventions* ce groupe de systèmes d'unités se rattache aux formules *générales*:

$$\begin{array}{ll}
 (1) F = \delta \frac{mm'}{r^2} & (6) F = \beta [\mathbf{B} \cdot \mathbf{Id}l] \\
 (2) \mathbf{M} = \gamma (\mathbf{SI}) & (7) C = \beta [\mathbf{B} \cdot \mathbf{SI}] \\
 (3) \mathbf{A} = \frac{d\mathbf{M}}{dV} & (8) C = \frac{\beta}{\gamma} [\mathbf{B} \cdot \mathbf{M}] \\
 (4) \oint (\mathbf{B}, d\mathbf{l}) = \alpha \mathbf{I} & (9) \mathbf{B}_2 = \mathbf{B}_0 + \alpha \mathbf{A}' / \gamma \\
 (5) E = -\beta \frac{d}{dt} \iint \mathbf{B}_N ds & \text{avec } \alpha\beta = 4\pi\gamma^2\delta.
 \end{array}$$

La première de ces conventions consiste à dire que l'on entend ne pas mesurer toujours une induction avec la même unité: on emploie en effet deux unités différentes dont la deuxième est, disons,  $\lambda$  fois plus grande par exemple que la première.

On convient alors d'employer la première unité, en conservant la notation  $\mathbf{B}$ , pour les expériences auxquelles correspondent les formules (5), (6) et (7), tandis que l'on utilise la deuxième unité, en remplaçant  $\mathbf{B}$  par  $(\lambda\mathbf{H})$  dans les formules (4) et (8). Enfin, dans l'égalité (9), on emploie la première unité pour le premier membre et la seconde unité pour le deuxième membre.

On a en outre l'habitude de substituer la notation  $1/\mu_0$  à la notation  $\delta$  que nous avions utilisée dans l'expression de la loi de Coulomb\*.

Ces diverses conventions font que nos égalités générales deviennent:

$$\begin{array}{ll}
 (1) F = mm' / \mu_0 r^2 & (6) F = \beta [\mathbf{B} \cdot \mathbf{Id}l] \\
 (2) \mathbf{M} = \gamma (\mathbf{SI}) & (7) C = \beta [\mathbf{B} \cdot \mathbf{SI}] \\
 (3) \mathbf{A} = \frac{d\mathbf{M}}{dV} & (8) C = \frac{\beta\lambda}{\gamma} [\mathbf{H} \cdot \mathbf{M}] \\
 (4) \oint (\mathbf{H}, d\mathbf{l}) = \alpha \mathbf{I} / \lambda & (9) \mathbf{B} = \lambda \mathbf{H} + \alpha \mathbf{A}' / \gamma \\
 (5) E = -\beta \frac{d}{dt} \iint \mathbf{B}_N ds & \text{avec } \alpha\beta = 4\pi\gamma^2 / \mu_0.
 \end{array}$$

On arrive enfin aux règles de coordination d'unités indiquées au début de cette note en décidant (arbitrairement) que l'on donne la valeur  $4\pi$  au coefficient numérique  $\alpha/\lambda$  de la formule (4) et la valeur  $UN$  aux coefficients numériques  $\beta$  et  $\beta\lambda/\gamma$  des égalités (5), (6), (7) et (8); cela revient à dire que l'on écrit *a priori*:

$$\alpha = 4\pi\mu_0; \quad \beta = 1; \quad \gamma = \mu_0; \quad \lambda = \mu_0.$$

C'est en raison de ces conventions que les deux *inductions* qui servent successivement d'unités de mesures aux *inductions*  $\mathbf{B}$  et  $\mathbf{H}$  peuvent se trouver rattachées séparément de manière différente aux unités fondamentales, comme cela se produit, par exemple, dans les systèmes d'unités électrostatiques.

\* On sait que l'emploi de la notation  $\mu_0$  dans l'expression de la loi de Coulomb est un résidu de l'idée ancienne, *mais reconnue inexacte*, que l'on pouvait représenter les phénomènes magnétiques par une série de lois de Coulomb comportant chacune un coefficient d'attraction  $\mu$  qui aurait dépendu de la nature du milieu ambiant. Le coefficient  $\mu_0$  était alors celui qui correspondait au vide.



## VI. THE FORCE BETWEEN TWO ELEMENTS OF CURRENT\*

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ACCORDING to Ampère, the attraction between two elements of current  $i ds$  and  $i' ds'$  is

$$dF = \frac{2\mu}{r^2} \left( \cos \epsilon - \frac{3}{2} \cos \theta \cos \theta' \right) i i' ds ds' \quad \dots\dots(I),$$

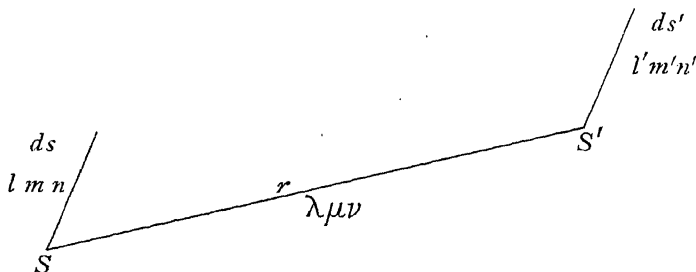
where  $r$  is the distance between the elements,  $\epsilon$  the angle between them, and  $\theta$  and  $\theta'$  the angles between  $r$  and  $ds$ , and  $r$  and  $ds'$  respectively.

When the element  $ds$  forms part of a closed circuit, the total force on  $ds'$  is the resultant of forces

$$\mu i' ds' \sin \phi' \cdot i \sin \theta ds / r^2.$$

Each elementary force acts at right angles to the plane containing  $r$  and  $ds$ , and  $\phi'$  is the angle between  $ds'$  and this direction.

It may be convenient to give here a proof of this statement.



In the figure,  $xyz$  and  $x'y'z'$  are the coordinates of  $ds$  and  $ds'$  respectively,  $lmn$  and  $l'm'n'$  their direction cosines,  $\lambda\mu\nu$  the direction cosines of  $r$ .

The point  $S'$  is fixed while  $S$  moves round a circuit  $S$ .

Then 
$$\frac{d}{ds} \left( \frac{1}{r} \right) = -\frac{1}{r^2} \frac{dr}{ds} = \frac{1}{r^2} \cos \theta.$$

But 
$$r^2 = (x' - x)^2 + (y' - y)^2 + (z' - z)^2,$$

whence 
$$\frac{dr}{dx} = -\frac{x' - x}{r} = -\lambda,$$

and similarly 
$$\frac{dr}{dy} = -\mu, \quad \frac{dr}{dz} = -\nu.$$

\* An investigation leading from Ampère's expression to a result similar to that obtained here is given in Mascart and Joubert, *Leçons d'Électricité*, Part 3, Chap. II.

Again

$$\begin{aligned}\frac{d\lambda}{dx} &= \frac{1}{r} - \frac{x' - x}{r^2} \frac{dr}{dx} = -\frac{1}{r} + \lambda \frac{\lambda}{r}, \\ \frac{d\lambda}{dy} &= \mu \frac{\lambda}{r}, \quad \frac{d\lambda}{dz} = \nu \frac{\lambda}{r}, \\ \frac{d\lambda}{ds} &= \left( -\frac{1}{r} + \lambda \frac{\lambda}{r} \right) l + \frac{\mu\lambda}{r} m + \frac{\nu\lambda}{r} n \\ &= -\frac{l}{r} + \frac{\lambda}{r} \cos \theta\end{aligned}$$

Again  $\cos \theta' = l'\lambda + m'\mu + n'\nu$

$$\begin{aligned}\frac{d(\cos \theta')}{ds} &= l' \left( -\frac{l}{r} + \frac{\lambda}{r} \cos \theta \right) + m' \left( -\frac{m}{r} + \frac{\mu}{r} \cos \theta \right) + n' \left( -\frac{n}{r} + \frac{\nu}{r} \cos \theta \right) \\ &= -\frac{\cos \epsilon}{r} + \frac{\cos \theta \cos \theta'}{r}\end{aligned}$$

$$\begin{aligned}\frac{d}{ds} \left( \frac{\lambda \cos \theta'}{r} \right) &= \lambda \cos \theta' \frac{d}{ds} \left( \frac{1}{r} \right) + \frac{\cos \theta'}{r} \frac{d\lambda}{ds} + \frac{\lambda}{r} \frac{d(\cos \theta')}{ds} \\ &= \frac{3\lambda \cos \theta \cos \theta'}{r^2} - \frac{l \cos \theta'}{r^2} - \frac{\lambda \cos \epsilon}{r^2}.\end{aligned}$$

$$\therefore \int \left( \frac{\lambda \cos \epsilon}{r^2} - \frac{3\lambda \cos \theta \cos \theta'}{r^2} \right) ds = - \int \frac{l \cos \theta'}{r^2} ds - \int d \left( \frac{\lambda \cos \theta'}{r} \right).$$

The last integral vanishes when taken round the complete circuit  $S$ , whence

$$\frac{\lambda}{r^2} (\cos \epsilon - 3 \cos \theta \cos \theta') ds = - \int \frac{l \cos \theta'}{r^2} ds \quad \dots\dots(2).$$

Ampère's expression for the attraction along  $SS'$  is given by (1). For unit currents the component  $f_x$  along the  $x$  axis is

$$f_x = -\lambda dF = -\frac{\lambda \cos \epsilon}{r} \mu ds ds' - \frac{\lambda}{r^2} (\cos \epsilon - 3 \cos \theta \cos \theta') \mu ds ds'.$$

Integrating round the circuit  $s$ , and making use of (2), we find

$$\begin{aligned}f_x &= \mu ds' \int \left( \frac{l \cos \theta'}{r^2} - \frac{\lambda \cos \epsilon}{r^2} \right) ds \\ &= \mu ds' \{ l (\lambda l' + \mu m' + \nu n') - \lambda (l l' + m m' + n n') \} ds / r^2 \\ &= \mu ds' \{ (\nu l - \lambda n) n' - (\lambda m - \mu l) m' \} ds / r^2.\end{aligned}$$

But if the plane containing  $r$  and  $ds$  has direction cosines  $L, M, N$ ,

$$(\mu n - \nu m) / L = (\nu l - \lambda n) / M = (\lambda m - \mu l) / N = \sin \theta.$$

Hence

$$f_x = \mu ds' \int (M n' - N m') \sin \theta ds / r^2 \quad \dots\dots(3).$$

Call  $\phi'$  the angle between the direction  $LMN$  and  $ds'$ , and  $\xi, \eta, \zeta$  the direction cosines of the plane containing  $LMN$  and  $ds'$ . Then

$$\frac{M n' - N m'}{\zeta} = \sin \phi',$$

and

$$f_x = \mu ds' \int \xi \sin \phi' \frac{\sin \theta ds}{r^2},$$

which leads to the result stated above, viz. that the force exerted on the element  $ds'$  by the closed circuit  $s$  is the resultant of forces

$$\mu ds' \sin \phi' \cdot \sin \theta ds/r^2.$$

Let

$$B_x = \mu \int (L \sin \theta / r^2) ds,$$

and let  $B_y$  and  $B_z$  be obtained by replacing  $L$  by  $M$  and  $N$  respectively in the above integral. The resultant  $\bar{B}$  of  $B_x$ ,  $B_y$ ,  $B_z$  is the magnetic intensity; its direction cosines  $\bar{L}$ ,  $\bar{M}$ ,  $\bar{N}$  are equal to  $B_x/\bar{B}$ , etc.

Substituting in (3) we have

$$f_x = ds' (B_y n' - B_z m') = \bar{B} (\bar{M} n' - \bar{N} m') ds'.$$

Denoting by  $\psi$  the angle between  $\bar{B}$  and  $ds'$ , and by  $\Xi$ ,  $H$ ,  $Z$ , the direction cosines of the plane containing them, we have

$$f_x = \Xi \bar{B} \sin \psi ds',$$

which leads to the well-known theorem that the resultant is a force  $\bar{B} \sin \psi ds'$  in the direction perpendicular to  $\bar{B}$  and to  $ds'$ .

